# CALCAREOUS CEMENTS:

## THEIR NATURE, MANUFACTURE, AND USES.

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BY

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# PREFACE.

In looking over the prefaces to the two former editions, it is impossible to avoid some reflections upon the wonderful changes which have manifested themselves in the Cement industry since this book was written in 1895. At that time cement users, in spite of the great improvements effected in consequence of the publication of the tests of Mr. J. Grant, in 1871, were content to employ a material which frequently contained as much as 20 per cent of inert particles. The introduction of fine grinding, which now has been brought to a great pitch of perfection, necessitated important changes in the plant, while the use of the rotary kiln and the tube mill have involved the transfer to the scrap heap of many of the mechanical appliances formerly regarded as essential to the manufacture. We have consistently urged the need of some uniform system of cement-testing, and we hailed the publication of the British Standard Specification for the testing of Portland cement with much pleasure, as we were convinced that its adoption would be of material advantage both to manufacturers and consumers.

On the subject of the chemistry of cement action, in spite of much patient investigation along many different lines, we are unable to claim a perfect knowledge of the reactions involved both in the kiln and in the setting of the cement, but it may safely be affirmed that these questions are now much nearer solution than at the date of the last edition of this work.

We looked forward at that period to great extension in the use of cement concrete, in consequence of the employment of metallic reinforcement, and though our progress in the new system of construction has been less rapid than that of some of our continental rivals, we are confident that reinforced concrete has a great future before it for buildings of every kind. We are still far from a complete knowledge of the possibilities of these structural materials,

but every year will bring increased confidence in the value and durability of steel framework and Portland cement concrete rightly applied.

For the past three years copies of this book have been unprocurable, as the difficulties of printing were acute, but the authors have endeavoured to bring the work in line with modern requirements in manufacturing operations. Revision has involved the discarding of many of the chapters that had value in the last edition but which have had to make room for new developments, whilst several chapters have been wholly rewritten and provided with new illustrations. We are indebted to the publishers for resetting the work throughout, and our thanks are given also to manufacturers and others for readily granting permission to illustrate their inventions, as well as for supplying valuable details of most recent improvements.

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# CALCAREOUS CEMENTS:

## THEIR NATURE, MANUFACTURE, TESTING AND USES.

## CHAPTER I.

### INTRODUCTION.

CONTENTS.—Antiquity of Use of Lime—Definition of Cements and Limes—Slaking—Quicklime—Calcination of Limestone—Classification of Limes—Action of Carbon Dioxide—Influence of Clayey Matters—Pozzolana, Trass, etc.—Silica and its Compounds—Alumina—Condition of the Silica Important—Analyses of Hydraulic Limestones and Lime—Dorking Stone Lime—Influence of Alkalies.

**Antiquity of the Use of Lime.**—The practice of employing limes as binding agents for stones, bricks, and other similar materials used in construction is one of great antiquity, and the Romans, the most mighty builders of the ancient world, were well acquainted with the use of limes, as also with certain of the methods of improving fat or pure limes, in order to impart to them cementitious and hydraulic properties.

**Definition of Cements and Limes.**—" Cements," as distinguished from limes, are materials which are capable of solidifying when in contact with water without perceptible change of volume, or notable evolution of heat; " hydraulic cements and limes " are such as possess the power of " setting " or solidifying under water. All limes have a tendency to expand and to fall asunder, or to crumble into powder when treated with water, and are said to become " slaked." The purer the lime the more energetic and rapid is this action, while conversely the greater the quantity of clayey matter combined with the lime, the less intense, as a rule, is the chemical affinity for water, and the slower is the act of hydration, and to this extent the greater is the resemblance of such limes to cements. " Limes," therefore, as distinguished from cements, " fall " or crumble when exposed to the action of water.

It may be as well to point out here that the above definitions, though they do not entirely accord with all the previous theories of limes and cements, are those which will be adopted in the present work.

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**Combination of Lime with Water.**—The chemical affinity of lime for water is one of the most powerful with which we are acquainted, and " quicklime " (calcium oxide), or lime recently calcined, when exposed to the air speedily attracts moisture from the atmosphere, and combines with such water to form calcium hydroxide, or slaked lime. This hydroxide may occupy as much as three times the space previously filled by the quicklime, and, therefore, the amount of slaked lime produced from a given bulk of quicklime appears, in certain cases, to be very considerable.

**The Speed of Slaking.**—Some writers have attempted to classify the different varieties of lime in accordance with the quantity of slaked lime produced, or with the speed with which they were observed to combine with water ; but it is now known that this slaking action depends upon numerous conditions which have to be specially studied for each class of limes, and that any general deductions founded upon the act of hydration alone are likely to be inaccurate and misleading.

**Intermediate Limes.**—Certain impure limes, resembling in their composition the constitution of cements, have been appropriately named " intermediate limes," or such as occupy a position intermediate between the true limes, which undergo disruption when exposed to the action of water, and the cements which do not, apparently, become changed when so treated.

It may be assumed that limes of every different degree of energy, from pure oxide of calcium down to true calcareous cements, exist in nature ; thus there is an enormous range of varieties of action to be studied, and any attempt to classify all limes under two or three sub-heads must be futile and untrustworthy.

In order to understand rightly the action of limes and cements, a certain amount of chemical knowledge is involved, and this branch of the subject may now be briefly discussed.

**Quicklime or Caustic Lime.**—Quicklime, caustic lime, or the oxide of calcium, one of the earthy metals, does not exist in nature, nor is metallic calcium itself anywhere found in an uncombined form. We obtain quicklime, the chemical symbol for which is $CaO$, by calcining or heating to redness a carbonate of lime, $CaCO_3$. and by this means expelling the carbonic acid gas or carbon dioxide, $CO_2$, with which the lime is combined, and which can be driven off in the gaseous form at a temperature of 1,000° C.

*Preparation of Quicklime.*—Lime combined with carbonic acid is found in a great variety of rocks in all parts of the world, and in every different degree of purity. From any pure carbonate of lime, such as marble, or from any of the various descriptions of limestone and of chalk, the calcium oxide or quicklime can thus readily be prepared ; but, in order to keep the oxide unchanged, it must, as already stated, be preserved from contact with the atmosphere.

**Chemical Composition of Quicklime.**—In a pure carbonate of lime 44 parts weight of carbon dioxide or carbonic acid are combined with 56 parts weight of calcium oxide. In the oxide itself 40 parts by weight of metallic ;ium, Ca, are combined with 16 parts of oxygen gas, O. This oxide not be decomposed by heat. The lime burner has, therefore, in his kilns irive off the combined carbonic acid in the form of a gas, and thus to ain the lime as used by the builder.

**Calcination of Limestone.**—Generally speaking, the limestone or chalk, n placed in the kiln, contains a certain percentage of moisture, which also to be expelled, and thus the lime burner can rarely, when the e is thoroughly well burned and all the carbon dioxide is expelled, ain more than half its weight of quicklime from a given weight of stone lt with in the kiln, though in theory the yield should be 56 per cent. of .

Carbonic acid gas is driven off much more freely in an atmosphere of m, and for this reason some authorities have advised the use of the m jet in lime kilns, but we are not aware that this plan has met with measure of practical success.

**Action of Aqueous Vapour.**—The action of aqueous vapour upon the ; undergoing calcination may be thus explained:—A vapour or gas nds into a space already occupied by another gas differing from it in position, almost as quickly as it would into a vacuum, owing to the of the diffusion of gases, which teaches us that the various gases have a powerful tendency to permeate each other, that, in order to do so, will frequently overcome considerable resistance. Water, for example, orates as readily into dry air as into a vacuum, but this tendency is eded when the air above it is already charged with aqueous vapour. he same way when the red-hot lime is giving off carbonic acid gas, this escapes much more freely into an atmosphere of aqueous vapour than one of carbonic acid gas, for in this latter case the escaping carbonic has to overcome the pressure of that which has been already evolved. true that if we could substitute a current of air at a very high tempera- for the aqueous vapour the result would be the same, but this would il practical difficulties.

**Gay-Lussac's Experiment.**—Gay-Lussac, the eminent chemist, devised ngenious experiment to demonstrate the effect of steam upon the cal- tion of lime. He introduced into a hard glass tube, inserted in a furnace h enabled it to be raised to the required temperature, some pieces of :en marble. One end of the tube was connected with an apparatus he evolution of steam, and the other end was furnished with a contrivance :ollecting the carbonic acid gas. The temperature was then raised to point at which the marble began to be rapidly decomposed, and at this by checking the draught the mass was reduced to a dark red heat,

so that all evolution of carbonic acid ceased. Steam was at this moment permitted to pass through the tube, and at once carbonic acid gas again made its appearance in considerable quantities, and continued to pass off under these circumstances in a manner entirely dependent upon the current of vapour. This experiment proves that limestone is decomposed at a far lower temperature with the help of aqueous vapour than under ordinary circumstances. In an atmosphere of carbonic acid gas, carbonate of lime, as we know from the investigations of Faraday and Hall, remains unchanged even at a full red heat.

**Composition of Slaked Lime.**—When lime becomes "slaked" it is found that 56 parts by weight of quicklime combine with 18 parts by weight of water, $H_2O$, to form 74 parts of calcium hydroxide, $Ca(OH)_2$. Great heat is evolved in this process, and the action is expedited by the use of boiling water. Certain "poor limes," which will scarcely slake or fall to powder when cold water is employed, will crumble into dust readily if the water is at the boiling point.

**Classification of Limes.**—Limes are frequently classed as "fat" or rich limes, if they readily become slaked and furnish a large volume of powder, and "poor" if they are impure and become slaked slowly, yielding relatively but little dust. Cases occur, of course, when the lime will not fall or slake at all. Certain poor limes, which are practically natural cements, may, if they are calcined at a proper temperature and are finely ground, be employed as cements. To render these limes available for the use of the builder, it is thus necessary that they should be ground previous to use.

**Condition of Water in Slaked Lime.**—The water which combines with the lime in the act of hydration is truly solidified, and the hydrate formed is, when the exact proportion of water necessary for this purpose has been employed, an absolutely dry powder. On adding a further quantity of water, the bulk of this powder is much reduced, and it may be tempered into an extremely rich and unctuous paste. If this paste is permitted to dry, it shrinks and forms a porous mass of no great hardness.

**Dry Slaked Lime kept from Air remains Unchanged.**—If the hydrate of lime is preserved from atmospheric action and placed in a hermetically sealed vessel, either as a dry powder or made up with water, it undergoes no alteration whatever, the powder remaining as such for an indefinite period, and the paste showing no sign of change. The hydrate of lime possesses in fact no inherent power of solidification. In proof of this, Alberti states that some lime taken from a mortar-pit in an old ditch, abandoned for upwards of 500 years, was "still so moist, well tempered, and ripe that not honey nor the marrow of animals could be more so."

**Lime slowly recombines with Carbonic Acid.**—When exposed to the air, pure caustic lime is converted very slowly and without notable increase of temperature into a rather coarse powder. It is not, under these circum-

stances, wholly converted into a carbonate of lime, even after the lapse of many years, but, by the simultaneous absorption of moisture and carbonic acid, it is resolved into a double compound having the formula, according to Fuchs, of $CaCO_3 + Ca(OH)_2$, or consisting of equal equivalents of the carbonate and the hydrate of lime. The carbonate thus produced would seem to result from the decomposition of the first-formed hydrate, for when moisture is wholly excluded no combination between the lime and the dry carbonic acid gas takes place. In order to expel the water of hydration, the slaked lime must again be heated to redness.

**The Action of Carbonic Acid mainly Superficial.**—Lime made from pure carbonate of lime, when slaked and used for mortar, likewise gradually recombines with the carbonic acid gas present in the atmosphere and becomes indurated, but this action is mainly in the superficial layers of the mortar, as the gas penetrates very slowly. In fact years must elapse before the recarbonisation of the lime is thoroughly accomplished, and in the case of thick walls the internal layers of mortar never become completely hard. It is necessary to distinguish between the so-called "set" of the mortar, which is merely due to the absorption of the superabundant water, and the actual induration by means of the carbonic acid gas, which is a process of years or of ages in the case of pure limes.

**The Influence of Clayey Matters.**—But absolutely pure limestones are only met with in exceptional cases, as nearly all limestone rocks and the greater part of the chalk formation contain varying percentages of clayey matters (silicates of alumina), iron, alkalies, etc., and it is upon the proportion of these ingredients present that the behaviour of the calcined lime principally depends. It is, in fact, owing to the presence of certain of these clayey matters, first, as we shall see pointed out by Smeaton, that limes pass over by gradual stages into the form of cements—that is to say, that these substances so far influence the slaking action that they may even bring about the ultimate setting of the mixture without change of volume — the characteristic property (as already stated) of cements.

**Artificial Admixture of Clayey Matters.**—It is not necessary, however, that the limestone should have been the source from which these clayey matters were derived; they may be conveyed to the calcined lime by admixture with it at the time when it is treated with water, or they may be ground up along with the lump lime before it is slaked. It is this fact which needs careful consideration when we have to deal with the influence of heat on mixtures of lime and clay, and the nature of the changes effected in the kiln. The silica compounds are of a very complex character, and may be produced, as we shall see, both by heat and in the humid way. All that is necessary for the due action of these clayey matters is that they should themselves have been roasted or calcined, either artificially or by volcanic heat.

**Pozzolana, Trass, etc.**—Certain of these substances which are added to pure limes to bring about this action, are called pozzolanas or trass. These are clayey or siliceous matters of volcanic origin, but roasted shales, brick-dust, and burnt clay or ballast, all of them more or less possess this influence on the pure limes, and have the power of imparting to them the attributes of cements.

The volcanic ash found in the Island of Santorin, and known as Santorin earth, is typical of many kinds of scoriæ which have been used successfully to impart to limes hydraulic properties. The proportion of silicate of alumina in this is relatively high, and there is much less iron than in the case of trass and pozzolana. The value of all these substances depends on the soluble silica they contain, but this has been rarely shown in published analyses. Schoch * gives the following analyses of trass by Michaelis, remarking that the content of soluble silica in these samples is low, and that in his own experience he found it to vary from 18 to 21 per cent. He mentions two samples that contained 28 and 36 per cent. respectively.

|  | Yellow Trass | Blue Trass |
|---|---|---|
| Silica,*   .   .   .   .   .   .   . | 60·345 | 59·172 |
| Alumina,   .   .   .   .   .   . | 19·414 | 20·462 |
| Oxide of iron,  .   .   .   .   . | 4·749 | 5·179 |
| Oxide of manganese,   .   .   .   . | 0·913 | 0·448 |
| Lime,   .   .   .   .   .   . | 2·177 | 2·783 |
| Magnesia,   .   .   .   .   . | 1·604 | 1·985 |
| Potash,   .   .   .   .   .   . | 5·447 | 4·669 |
| Soda,   .   .   .   .   .   . | 4·271 | 4·931 |
| Sulphuric acid,   .   .   .   .   . | 1·131 | 0·525 |
|  | 100·051 | 100·154 |
| * Containing free hydrated silica, soluble in solution of carbonate of soda,   .   .   .   . | 8·540 | 9·067 |

**Silica and its Compounds.**—It will be necessary, in order to understand the chemistry of cements, to treat next of silica and its compounds. Silica, the oxide of the element silicon, is found very widely distributed in nature, sometimes pure, but more often in combination with other substances, as it possesses strong affinity for entering into the composition of complex salts, known as compound silicates. It plays the part of an acid, and combines with lime, alumina, iron, and the alkalies in a vast number of different proportions. It is found that 28 parts by weight of silicon, Si, and 32 parts by weight of oxygen, are present in silicic acid or silica, having the chemical formula of $SiO_2$. Clay, the silicate of alumina, may be taken as the type

* *Die Aufbereitung der Mörtelmaterialen*, 3rd Ed., p. 37.

of the silica compounds, while Quartz, flint, and chalcedony consist of almost pure silica. Porcelain clay, which contains about 47 parts per cent. of silica, 39·2 parts of alumina, $Al_2O_3$, and 13·7 parts of water, and corresponds to the chemical formula $Al_2O_3\ 2SiO_2 + 2Aq$, with a molecular weight of 258·4, may represent the silicates. There are, however, an enormous number of clays in which silica and alumina are present in very varying proportions, and which contain in addition iron, alkaline matters, lime, etc. For certain of these clays it becomes almost impossible to propound any reliable chemical formula, to express their composition ; and alumina, while it may combine in certain definite proportions with the silica as a base, is also capable of acting as an acid, and of combining with lime and the alkalies to form certain more or less unstable compounds termed aluminates.

**Alumina** is the oxide of the metal aluminium, Al, which has the atomic weight of 27·2, and 2 parts of aluminium combine with 3 parts of oxygen, equal to 48, to form its only known oxide, termed alumina, the molecular weight of which is 102·4.

It will not now be necessary to study in detail the combinations of silica and alumina with iron and the alkalies—soda and potash—though these compounds play a very important part in cement action ; we shall have to revert to this question hereafter when we consider the chemical changes consequent on the hydration and induration of cements of various kinds.

Restricting ourselves for the present, therefore, to the silicates of alumina, as typical of the compounds of silicic acid, we may pass on to discuss the modifications brought about in the slaking action of limes consequent upon the presence of these substances. We will take first impure limestones, or such as contain a proportion of the silicate of alumina, together with certain percentages of the oxides of iron tending to discolour the lime.

**Influence of Heat on the Silicates.**—When limes of this character—namely, such as are combined with varying percentages of silicates—are burnt in the ordinary way in the kiln, the carbonic acid gas is first expelled from them, as in the case of the pure limestones, and the clayey matters assist in its expulsion, owing partly to the affinity of the silicic acid for the lime, and partly to the fact that the free and combined water in the clay is driven off, and the steam produced in this way facilitates, as already stated, the expulsion of the carbonic acid. There is thus a double change to be effected in the kiln, and the expulsion of the water from the hydrated silicate of alumina in the clay may go on side by side with the dispersal of the carbonic acid.

**The Calcination of Clayey Limestones.**—These clayey limestones are thus burnt more readily than the pure limestones ; they also require less fuel and less time. But when the heat is sufficiently prolonged, a further action takes place in the kiln, the silicic acid and the lime react upon one

another, and either produce a new compound, termed silicate of lime, or so far further the formation of such a silicate that, on the addition of water, this compound is formed with great rapidity. The silica combined with alumina and iron in the clay is free to pass to the lime as soon as the carbonic acid is expelled, and no doubt portions of the silica are seized upon by the red-hot lime, which is in what chemists term the "nascent state," and is, therefore, in a condition eminently well fitted to form fresh chemical compounds. In a similar way the alumina and the iron act as feeble acids, and combine with a portion of the lime to form aluminates and ferrites of lime at the temperatures found in the cement kiln. The calcined mass, if it is then brought into a very finely-divided condition, can readily be acted upon by water.

**Action of Water on Silicates formed in the Kiln.**—In using, for structural purposes, limes of this character, therefore, a fresh set of affinities comes into play. We have, first, the affinity of the quicklime for water, and, secondly, the affinity of the hydrate of lime and the silica and alumina to enter into combination. It must be pointed out that this second reaction can and does greatly change the violence of the affinity of lime for water, and that it is possible to so "deaden," if we may thus term it, the action of quicklime that, upon the addition of water, instead of heating up and falling into powder, it may pass (as we have seen) into the condition of a hydrated silicate, without perceptible heat, and with little or no change of physical condition.

**Stable Compounds formed by Hydration.**—The hydrated silicates of lime thus produced are not liable to be altered to any appreciable extent when exposed to the prolonged action of water or of the atmosphere, and the compounds of lime with silica and alumina thus afford a durable cementing material, suitable also for hydraulic purposes. It must not be forgotten that the lime which enters into combination with the silicic acid, passes from a slightly soluble into an almost completely insoluble condition, and it will be observed that the action of induration differs entirely, in the case of cements, from the slow and tedious hardening of common lime mortar, due to the gradual recombination of the lime with the carbonic acid gas present in the atmosphere.

**Character of the Kiln Changes.**—It will have been noticed that we were careful to state that the lime, together with the silica, the alumina, and the iron, either entered directly into fresh chemical combinations, or that they tended to promote the formation of silicates and other compounds; for the changes brought about in the kiln, and the subsequent reactions which take place when water is added to the calcined materials are very complex and difficult to investigate. It is evident from very simple tests that, even in the case of cements of the Portland type, considerable quantities of lime remain in a condition under which they are capable of combining immediately with

water, or in a state in which such lime is free to be acted upon or to undergo further chemical change. In a well-burnt sample of intermediate lime the silica has assumed that form in which it is soluble in a boiling solution of carbonate of soda, after treatment with hydrochloric acid, since clay which has been calcined in contact with lime or other metallic oxides is readily attacked by the acid, and the silica liberated assumes the gelatinous condition, or that in which it can freely combine with the alkalies. During the calcination, therefore, of hydraulic limes a stage is reached when, after the expulsion of the carbonic acid, the silica and the alumina of the clay on the one hand, and the lime on the other, are in a condition to react mutually upon one another, and to form compounds capable of being re-arranged in the presence of water. The most recent opinion is that in well-made samples of Portland cement we have a tri-calcic silicate in conjunction with a tri-calcic aluminate. If a small quantity of the lime present is combined with the iron as a calcic ferrite, these compounds would together account for the whole of the lime present in the original mixture. We are not able to state very definitely the proportions of these combinations, but this fact is certain, that at this period of the calcining process a very slight increase of heat suffices to fuse or partially vitrify the mass, in which case complete combination between the lime and silica has undoubtedly taken place, and the silicates produced in this way by heat manifest but little tendency to undergo any change when treated with water. It is, therefore, more important not to overburn or, as it is termed, to " clinker " these intermediate limes, though in the manufacture of Portland cement it is essential that the stage of incipient fusion should be attained in the kiln.

**Action of Impure Limestones when Calcined.**—Some clayey limestones are much more liable to fuse than others, and it has been pointed out that those in which the proportion of iron and of the alkalies is large are most exposed to this risk. The glass-like or vitreous silicates formed in this way by heat are generally produced only on the surface of the lumps of overburnt lime, and unless such lumps are carefully picked out and cast aside when the lime is being made into mortar, they may be the source of much subsequent injury to the work, first by the retarded slaking of particles of lime encased in the inert silicates, and second by the more gradual hydration of certain of these complex silicates, which reaction may be attended by slight increase in bulk, tending to the disruption of the mass.

**Limes vary widely in their Behaviour with Water.**—It will be understood that, between the pure or fat limes which slake in the ordinary way, and the true cements which set without change of volume, there are an infinite number of varieties of limes which incline in one direction or the other towards these two extremes. There are also numerous hydraulic limes which first fall to pieces during the act of hydration, and which subsequently set and become indurated when the effect of the silicates comes into play. To

this category belong many of the limes of the lias formation, and certain of the gray limes of the lower chalk.

**Definition of the Energy of Cement Action.**—The energy of a cement depends upon the rapidity with which the lime and the silica, or the lime and the alumina, combine in the presence of water to form stable compounds, or with which the ready-formed silicates and aluminates become hydrated when water is added. We have thus the quick-setting cements of the Roman cement type, which become indurated mainly by simple hydration in a few minutes, and the dense cements resembling Portland, which depend for their induration on a re-arrangement of the silicates, and which may take as many hours to set as the former substance does minutes.

It should be here noted that when we speak of the setting of cements we imply the act of induration, and not the mere absorption of the water, which is most characteristic of the imperfect setting action of a lime mortar.

**The Influence of Calcination upon Cement Action.**—The calcination of these varieties of cements plays a very important part in their subsequent behaviour, when tempered with water. Thus it is possible from the same clay-limestone to prepare—

(a) A hydraulic lime ;
(b) A quick-setting cement ; and
(c) A cement resembling Portland cement in character.

At a low temperature in the kiln the mixtures of lime and clay have not mutually reacted the one on the other, and we obtain a material in which the energy due to the hydration of the lime overcomes the tendency of the silicic acid to enter into combination with this lime, under the agency of water.

When the second stage in the calcination is reached the silicic acid is liberated or rendered capable of attacking the lime, yielding a cement which sets with comparative rapidity. While, lastly, under still more intense firing, the stage of calcination is approached when silicates and aluminates are formed in the kiln, and when the material acts like a Portland cement, and when the iron, moreover, which had during the first and second degrees of calcination remained in the condition of a peroxide, passes into that of a protoxide (as is always the case in perfectly prepared Portland cement). This change in the oxide of iron is only effected at very high temperatures, and furnishes a certain indication of the production of a dense slow-setting cement. If, in the case of this clayey limestone, the clay had been less in quantity, we should have obtained a hydraulic lime which would slake with difficulty, and which would be liable to the evil effects of "after-slaking." If the proportion of the bases contained in the clay, relatively to the amount

of silicic acid present, had been greater, the mass would have probably become vitrified or partially fused before the temperature necessary for the final stage of calcination was reached.

**Condition of the Silica Important.**—The condition of the silica present in impure limestones has an important influence on their value when employed for the manufacture of hydraulic lime. It occurs in the free state in greater or less quantity, in all clays and clay limestones. If it exists in coarse grains as quartz sand, it is unacted upon by the lime at the comparatively low temperature of the kiln, and, consequently, after calcination, does not separate as a gelatinous bulky mass, as is usual with the silica in good hydraulic lime, when treated with hydrochloric acid. Further, it is not soluble in a boiling solution of sodium carbonate, and in this form is not in a condition to enter into combination, it is present in fact simply as inert matter, the lime consequently possessing no hydraulic properties. If, however, it occurs in an extremely fine state of division, it is acted upon by the lime at the temperature of the kiln, and is brought into the soluble form, but these siliceous limestones require a somewhat higher temperature for complete calcination than those which contain more alumina.

Many of the hydraulic limestones of France contain much free silica, in a very finely divided state. H. Le Chatelier gives the diameter of the spherical grains in the limestone of Teil as $\frac{1}{1000}$ of a millimetre. The Teil lime is held in high esteem in France, especially for marine work, on account of its low content of alumina. The following is its analysis :—

| | | |
|---|---|---:|
| Silica, | . . . . . . . . | 25·61 |
| Alumina, | . . . . . . . | 1·90 |
| Oxide of iron, | . . . . . . . | ·80 |
| Lime, | . . ` . . . . . | 70·60 |
| Magnesia, | . . . . . . . | 1·07 |
| | | 99·98 |

Some of the beds of impure limestone in the lower carboniferous formation contain free silica, as sand of somewhat coarse grain, in considerable quantity. Lime burned from stone of this description is easily recognised by its friable granular appearance, while, on the other hand, that which contains its silica in the soluble form, has a dense, close, even structure ; the lumps of quicklime give a ringing sound when struck together.

**Analyses of Hydraulic Limestones and Lime.**—In England the hydraulic limes are almost entirely supplied by certain beds of the lower chalk, and from the lias formation, that from the latter being the most esteemed. They have, however, been gradually falling into disuse, this being due to the continually increasing production of Portland cement and its low cost.

The following are analyses of blue lias hydraulic limestones of excellent

quality, No. 1, being from the neighbourhood of Newport, Monmouthshire, and No. 2 from Leicestershire :—

|  | No. 1. | No. 2. |
|---|---|---|
| Silica, . . . . . . . . | 7·311 | 9·680 |
| Alumina, . . . . . . . | 2·315 | 2·827 |
| Ferric oxide, . . . . . . . | ·530 | ·563 |
| Iron disulphide, . . . . . . | 1·149 | ·370 |
| Calcium carbonate, . . . . . . | 83·095 | 82·128 |
| Calcium sulphate, . . . . . . | ·275 | 2·122 |
| Calcium phosphate, . . . . . . | ·087 | .. |
| Magnesium carbonate, . . . . . | 3·605 | ·134 |
| Potash, . . . . . . . | ·597 ⎞ | Not |
| Soda, . . . . . . . . | ·318 ⎬ | determined |
| Loss on ignition, . . . . . . | ·834 ⎠ |  |
|  | 100·116 | 97·824 |

The following are analyses of the blue lias hydraulic lime of Leicestershire, No. 1 ground, No. 2 lump. The beds of stone burned for the preparation of the ground lime contain more clay than those used for the lump lime, and, after burning, the lime would either slake with difficulty, as described in the preceding paragraph, or it might not slake at all. When ground and stored for a short time, the material possesses the properties of a cement, setting and hardening without perceptible alteration in volume. Both of these limes have attained a deservedly high reputation as water limes :—

|  | No. 1. | No. 2. |
|---|---|---|
| Insoluble siliceous matter, . . . . | 3·603 | 1·031 |
| Silica, . . . . . . . | 17·496 | 12·230 |
| Ferric oxide, . . . . . . . | 8·972 | 2·907 |
| Alumina, . . . . . . . | 5·120 | 4·640 |
| Lime, . . . . . . . . | 57·393 | 72·980 |
| Magnesia, . . . . . . . | ·618 | 2·479 |
| Sulphuric acid, .. . . . . . | 3·153 | 1·775 |
| Potash, . . . . . . . | ·862 | ·641 |
| Soda, . . . . . . . . | ·346 | ·203 |
| Loss on ignition, . . . . . . | 2·480 | 1·062 |
|  | 100·043 | 99·948 |

**Dorking Stone Lime.**—Writers on building materials, and the authorities who are responsible for many of our most carefully drawn specifications, have with a surprising degree of unanimity concurred in calling the lime

prepared from the lower chalk in the vicinity of Dorking "stone lime." We have sought for some explanation of this fallacy, and offer the following suggestion :—Certain of the beds near Betchworth, and in the chalk hills eastward of Dorking, are much indurated and discoloured with iron salts, and a bed just between the chalk and the gault, known as firestone, is very hard, and is used locally for building. This indurated chalk is rejected by the lime-burners, as, owing to the high percentage of silica and alumina present therein, it yields a poor and very sluggish lime, but the raw material has certainly some pretensions to be called a stone. The lime prepared round Dorking is all burnt from chalk which contains from 5 to 10 per cent. of clay, and is of a pleasant buff tint.

Even Bartholomew, writing in 1840, is careful to point out that the "stone lime" of Dorking should be specified, and his precepts are still diligently followed by the conscientious architect who knows what he wants for the preparation of a good sample of mortar.

**The Influence of the Alkalies.**—Alkali salts are always present in small quantities in the clays used for cement-making, and in hydraulic lime-stones. They act as fluxes facilitating the reactions between the lime, alumina, and silica during the earlier stages of calcination, being partially volatilised when extreme temperatures are reached. They are only found in small quantities in well-burned cements, and have been supposed by some investigators to act as carriers of silicic acid to the lime and alumina in the presence of water, when the cement is gauged for use. If this view is a correct one, the same action would occur with the use of pozzolana or trass in mortar.

## CHAPTER II.

### THE BURNING OF LIME.

**Essential Conditions to be Observed.**—It will be evident, from the study of the chemical facts contained in the foregoing chapter, that the preparation of lime, for the builder or the farmer, is a very simple operation, and the process of lime-burning, though an art of the highest antiquity, has not received the same amount of care and attention as that devoted to the manufacture of cements. The lime-burner has merely to expel the carbonic acid, and he is not called upon to study the very complicated reactions involved in the production of cements.

**Antiquated Form of Kiln.**—The earliest lime-kilns were probably merely pits or hollows sunk in the ground, or excavated in the face of a bank or hillside, in which the limestone or chalk could be raised by the heat of burning coal, peat, wood, or other fuel, to the temperature needed to expel the carbonic acid. These crude kilns were often lined with some refractory material—brick or stone—and, where fuel was costly, devices were introduced to drive the heat through a considerable depth of the raw material, for which purpose a conical hood or chimney was added, and the body of the kiln or "shaft" was lengthened. The first kilns were doubtless of the intermittent type—i.e., the kiln charged with the raw material was burnt out and allowed to cool. The lime was then drawn out, and a fresh charge of raw material was introduced, to be in turn converted into lime. This process, in which there is a great waste of heat, is still in common use in many parts of the country, but in some places the old-fashioned kiln has given place to the so-called "draw kiln," or running kiln, in which the firing process is continuous, in order to effect which the total height of the kiln is greatly increased.

There is always, at the top of the draw kiln, a charge of raw materials, becoming gradually heated by the surplus heat from the calcination of the stone into lime in the central or hot zone, beneath which the calcined stone is in turn getting slowly cooled down so as to permit of its extraction at the bottom of the shaft as burnt lime.

**Forms of Continuous or Draw Kilns.**—Kilns of this type may, it is evident, be arranged as vertical shafts, or the heat may pass horizontally through a tunnel, one end of which is the firing end for the insertion of the raw stone and fuel, while the other end, nearest to the exhaust flue, or chimney, is used for the removal of the calcined material after being converted into lime. If a horizontally-fired kiln of this type is built in the form of a ring, we obtain the annular continuous kiln patented by Hoffmann ; or if the kiln is a mere straight tunnel, with a moving charge, we have the plan patented by Bock.

**Separation of the Fuel from the Lime Products.**—In order to obtain the lime free from admixture with the ash of the fuel, and thus to secure a material which shall present a better appearance and command a higher price, various plans of firing have been practised. They all aim at conveying the heat into the lime from a separate fire-chamber. The well-known " flare kilns," in use in the South of England for burning the chalk lime, are familiar examples of this principle, and in these kilns the fuel is burnt on fire bars beneath the charge. In loading the kiln, which has to be done by hand, rough arches are formed out of some of the larger lumps of chalk, so as to serve as fire-chambers, the heat from which strikes upwards throughout the entire mass, gradually converting the whole kiln-charge into lime. All kilns of this type involve the use of a rather larger quantity of fuel than those where the fuel is interstratified or mingled with the raw material.

**Shaft Kilns with Separate Fireplaces.**—Even in the case of running kilns or draw kilns, it is quite possible to provide fire-chambers surrounding the hot zone of the kiln, in which the fuel is consumed free from actual contact with the stone, and the products of combustion pass from the fireplaces into the central shaft. In some cases the kilns constructed on this plan are of very large dimensions, and the firing is so arranged that the amount of heat lost is very small. It is, however, evident that a certain amount of heat must pass into the walls of the fire-chamber, and thus lead to a waste of fuel, although a well-designed continuous kiln, with outside fires suitably disposed, will produce a pure clean lime, free from ash, at a relatively small cost.

**Advantage of Aqueous Vapour in the Kiln.**—The fact ascertained by Gay-Lussac, and mentioned on p. 3, that aqueous vapour may be made to play an important part in the expulsion of carbonic acid, should be remembered in connection with lime-burning. In nearly all cases the stone or raw material contains naturally a large proportion of moisture, but in some forms of vertical kilns all the moisture is driven off in the upper part of the kiln, before the hot zone, which is in the vicinity of the furnace chambers, is reached, and in such cases the burning can be to some extent facilitated by the introduction of steam into the kiln along with the air needed for

combustion. Experienced burners often wet the stone before burning it, which is a rough and ready way of attaining this object.

**Choice of Kilns for Limes of Different Kinds.**—The choice of a suitable kiln for burning the limestone must, to some extent, depend upon the chemical composition of the raw material. Certain of the hydraulic shales of the lias series, the chalk marls of Cambridgeshire, and the clayey limestones of the coal measures, are liable, if the calcination is conducted at too high a temperature, to become partially fused, and in this condition to cake together and to obstruct the draught; or, in running kilns, to cling to the walls of the kiln, and thus render the downward movement of the contents no longer possible. It is manifest that limestones of this kind require very great care in burning, and would be difficult to calcine in shaft kilns, unless special arrangements were provided for access to the heated mass in the vicinity of the firing zone. A kiln which is admirably adapted for burning a pure chalk or a mountain limestone would no doubt prove quite unsuitable for the calcination of these more fusible substances, and its introduction for this purpose would probably prove a failure.

**The Admixture with Ashes.**—For many purposes for which lime is used commercially, it is very important that it should be as pure as possible, and free from the ash or clinker arising from the fuel. It is perhaps less essential now than was formerly the case that the lime used by the builder should be kept apart from the ash of the fuel, as in nearly all important works it is customary to prepare the mortar in a mill, which would crush up these substances along with the lump lime and incorporate them in the mortar. For the use of the plasterer, the lime is slaked and run through a sieve, by which means all the impurities and underburnt particles are eliminated. A much better-looking lime no doubt results from the use of kilns in which all contact with the fuel is avoided; and although the cost of doing this adds, as we have seen, to the expense of the burning, it is certainly worth while to endeavour, if possible, to keep out the ash and clinker.

**Continuous Shaft Kilns.**—This fact has led to many recent inventions for kilns in which the lime is caused to pass down a shaft, and to be acted upon by furnaces or flames in the course of its progress. In nearly all of these kilns it becomes a matter of necessity to provide for a very considerable column of the material under treatment, because space is needed (a) for a charge of raw material to be dried and heated by the superabundant heat of the materials undergoing calcination in the hot part of the kiln; (b) for a stratum of limestone at the level of the furnaces, which must be maintained for some time at a bright red heat; and (c) for a space beneath the firing zone in which the lime can be cooled down sufficiently to permit of its removal at the lowest level. To work a kiln of this type with the utmost economy, it has been found that a total height of from 30 to 50 feet is needed. It is not expedient to increase the internal diameter to more than from 7 to 8 feet,

except in the case of a pure limestone ; and where the height of the shaft exceeds 40 feet, the process does not answer well, except with hard stone. The danger in the use of lofty kilns is the risk of the formation of pipes or chimneys, through which the draught rushes upwards with great rapidity, leaving a considerable part of the charge either in a raw state or very imperfectly calcined. When the wind happens to be direct on to the draw-holes, screens or shutters are needed to moderate the draught, and, unless in the hands of skilful and competent burners, lofty kilns are wasteful and unsatisfactory. In any case it will be found of advantage to provide for the admission of air all round the base of the kiln, and at several different levels, and means should be taken to enable the burner to control the air-inlets by the use of shutters or dampers.

**The Rüdersdorf Kiln.**—All writers on limes have described the draw kilns of Rüdersdorf, which are typical of many of the Continental attempts to reduce the amount of fuel needed for calcination. The kilns at Rüdersdorf are polygonal (5-or 6-sided) on plan, and consist of a central shaft which is composed of double truncated cones joined at the bases, the diameters of which vary from 7 feet at the narrowest part, at the top or charging level, to 10 feet at the broadest part of the hot zone, just above the fire-chambers. From this level the kiln-shaft contracts as an inverted cone to the base, where the calcined lime is extracted about every ten or twelve hours, in quantities of some 50 cwts. at a time. The fireplaces, which are constructed in the thick hollow walls of the kiln, are five or six in number, and communicate with the kiln-shaft by arched openings. The total height of the shaft is about 40 feet, and it is about 10 feet from the base to the level of the fire-chambers. Arched passages surround the base of the kiln, and into them openings are constructed to draw out the calcined lime. The thick walls of the kiln are carried up so as to form a level platform at the top, to which the stone is raised for charging purposes.

The proportion of fuel to burnt lime is set down at one to four. The fuel, which is very inferior coal, is burnt on firebrick perforated grates, and only the flame and products of combustion can enter the kiln-shaft. The ash falls into a pit beneath the fire-chambers, and is from time to time removed by special openings provided with shutters. In recent modifications of the Rüdersdorf kiln the fireplaces have given place to generators for producer-gas, while the shaft is provided with a cone or chimney like a Portland cement kiln, and the modern kilns are arranged for a much larger output, as much as 10 to 15 tons per diem in some cases. The coal consumption may range from 25 to 36 per cent. of the total output. The drawing takes place at regular intervals. The kiln introduced by Fahnehjelm is a recent type of this mode of construction. It is fired by means of gas produced in a generator.

**The Hoffmann and Dietzsch Kilns.**—The Hoffmann kiln has been used with excellent results for burning lime, both in this country and abroad,

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but, of course, in this case there is an unavoidable mixing of the ash of the fuel with the lime. One of these kilns at Rüdersdorf, near Berlin, said to be the largest in the world, has a daily capacity of 250 tons of lime.

In many parts of the Continent it is usual to burn bricks and lime in the same kiln. The Dietzsch kiln is also employed for burning lime. Descriptions of the above kilns will be found in the chapter dealing with the calcination of Portland cement in fixed kilns. Many of the kilns used for cement are also equally suitable for burning lime.

**The Rotary Kiln.** This kiln is in especial circumstances used for burning lime in the United States. It will be described in a later chapter treating of the burning of cement. An instance of its use for lime may be given. The limestones of Vermont contain from 98 to 99 per cent. of carbonate of lime and produce lime that has long been in high repute in New England. Some of the deposits are amorphous, and may be burned in the ordinary vertical kiln, others are crystalline and when heated break into fragments, impeding the draught, and thus rendering proper calcination impossible. The last-named beds supply marble, and the Vermont Marble Company also produce lime by the use of a rotary kiln 120 feet long, fired by producer gas. Spalls and unsuitable blocks from the quarries, and waste from the mills and workshops, are finely crushed, the crushed material is stored in bins from which it is fed to the kilns. One ton of coal produces from 3 to 4 tons of lime.

# CHAPTER III.

## HYDRATED OR SLAKED LIME.

CONTENTS.—Hydraulic Lime in France, Vicat's Researches—Hydraulic Index—The Process of Slaking—H. Le Chatelier's Theory of Hydration—Separation of the Hydrated Lime—Hydrated Lime in the United States—Specification of the American Society for Testing Materials for Hydrated Lime.

**Hydraulic Lime in France, Vicat's Researches.**—While the hydraulic limes in this country are supplied only as quicklime in lumps, or ground, in France they are delivered by the manufacturers in the state of hydrate and may be used as cements. France is rich in limestones. During the period extending from 1824 to 1845, J. L. Vicat investigated their location and properties, and published the result of his labours in two volumes.* In these are given the quarry or location, physical properties, geological formation, proportion of clay to carbonate of lime, nature of the clay, and the approximate content of carbonate of magnesia in 9,734 samples, found in 79 Départements. A considerable number of these possessed hydraulic properties in a greater or less degree, and their discovery resulted in a large production of hydraulic lime, which is extensively used in France to the present day. For many purposes, this lime has maintained its position in competition with Portland cement, and its continued use may be attributed to the care bestowed upon its preparation in the state of hydrate.

**Hydraulic Index.**—In France, the degree of hydraulicity of a lime is expressed by a number called the hydraulic index. This is obtained by adding together the percentage numbers of silica and alumina, and dividing by the percentage number of lime. The index may range from ·16 in the feebly hydraulic limes to ·5 in those eminently hydraulic.

**The Process of Slaking.**—The lime as drawn from the kilns is examined for insufficiently burned and over-burned or semi-vitrified portions, which are picked out, the latter being reserved for subsequent treatment. It is then spread in thin successive layers under sheds, or in silos, water being sprayed either upon each layer, or on the lime in the waggons as they are loaded from the kilns. The quantity required depends upon the composition of the lime, and may vary from 10 per cent. of its weight, if of a high index,

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* *Recherches statistiques sur les substances à chaux hydrauliques et à ciment naturel.* Two vols. Paris, 1839-1853.

to 20 per cent., if the index is low.  An excess of water is to be avoided, as it lowers the temperature and chills the lime, retarding the hydration.  This may result in a very dangerous product, which may cause the destruction of the work for which it is used.  The contents of the heaps or silos are allowed to remain until hydration is judged to be complete ; the time for this varies with the composition of the lime, and may be from 10 to 20 days or even longer.  In some modern works the silos are of large size, and are furnished with arrangements for automatically withdrawing the contents.

**H. Le Chatelier's Theory of Hydration.**—H. Le Chatelier [*] considers that the hydration of hydraulic lime takes place under four distinct phases.

(1) The porous lime near the surface of the heap absorbs the water sprayed upon it in consequence of its capillary attraction, and the water at first produces no chemical action, except upon the lightly burned portions or those with a low content of silica.  The quantity of water employed may be one and a half times that required by theory, or 10 to 15 per cent. of the weight of the lime, according to its character, this excess being necessary in consequence of the loss by evaporation, following the heating of the mass.  A greater excess of water, by lowering the temperature, prevents the complete hydration of the free lime.  Imperfectly hydrated lime is a very dangerous constituent in the finished product.

(2) During the hydration of succeeding layers, part of the water escapes in the state of vapour into the cooler mass below, but the whole of the lime is not hydrated, because the heat is sufficient to vapourise some of the water, and it is expelled before it has done its work.  Part of the water, however, assists the hydration of the unslaked portions.  To avoid loss of heat by radiation, the heap or silo should not be of smaller dimensions than 3 cubic metres.

(3) The mass now contains free lime and uncombined water, the latter in the state of vapour.  Hydration is still incomplete, especially in the case of hard burned limes rich in silica, for particles of free lime are imprisoned by the excess of silicate.  During this phase partial hydration of the silicates takes place.

(4) The process of hydration progresses continuously, and is effected by the action of the water combined with the silicates in the previous phase.  The formation and dissociation of hydrates is limited at any one temperature by a certain vapour tension proper for that temperature.  For calcium hydrate the tension of dissociation at 450° C. is 760 millimetres, with calcium silicate this tension is reached at 150°.  At ordinary atmospheric temperature the tension of dissociation of calcium hydrate is an inappreciable fraction of a millimetre, while that of the silicate reaches several millimetres.  At 100° the tension for calcium hydrate is still below 1 millimetre, while for the

silicate it is several centimetres. A transference of water from the silicates
to the hydrates must consequently take place, which continues until the
whole of the lime is hydrated, while obviously the rate of transfer increases
with the temperature. In the laboratory at 100° C., working on a small
scale, hydration is complete in about ten days, at ordinary temperatures
several months are needed. On the manufacturing scale it may require
from eight to fourteen days, with a good sample of lime. Prolonged hydra-
tion is, however, neglected in many works, forty-eight hours being considered
sufficiently long. This is certainly not long enough for well burned lime of
high index of silica, and the final result must be a very dangerous material,
liable to swell in use. If hydration is complete at the end of forty-eight
hours, the lime is either imperfectly burned, or it is deficient in silica. Careful
attention to the process of hydration results in a greatly improved product
without any material increase in cost.

**Separation of the Hydrated Lime.**—We have already seen that from the
same clay limestone three distinct products may be obtained, a hydraulic
lime, a quick-setting cement, and a cement resembling Portland cement
in character. All these are present in the burned and now hydrated lime,
their relative proportions depending on the chemical composition of the
stone and the temperature at which it has been burned. The usual practice
is to obtain from this mixture hydraulic lime and a natural cement of the
Portland type. The intermediate product, a quick-setting cement, is not
generally separated. There are many methods and arrangements of plant
for effecting this separation, but, whatever may be the ultimate product,
the first step in the process is to separate the fine from the coarse portion.
The material is passed over a grid, or through a revolving screen, to remove
large pieces, and then either through revolving sieves or air separators.
The fine portion is the chaux légère, or light lime, the coarse, a very hetero-
genous mixture, comprising unburned limestone, partially slaked lime, lime
soaked and hardened into lumps, and greyish-black hard grains, which
have all the properties of a cement. It is sometimes ground and mixed
with the light lime, but unless stored in silos for a prolonged period to com-
pletely hydrate the free lime, it is a very unreliable material. This process
is frequently employed with limes of low index, from which only a small
proportion suitable for cement could be obtained.

With limes of high index further separations are made. The residue
from the sieves is roughly ground, or really decorticated, the object being to
break up the softer portions and to remove adhering lime and the softer
silicates from the surface of the hard grains. It is sometimes submitted to
further slaking in silos before grinding. After grinding it is again sifted,
or separated, the fine portion is the chaux lourde, heavy lime; the coarse
portion, the grappiers, which when ground with the semi-vitrified lumps,
picked out of the lime before slaking, form the so-called " grappiers " cement.

This resembles Portland in character, but requires long storage in silos to render it perfectly sound and fit for use. The following are results of analyses by E. Léduc of a limestone and the three products obtained from it :--

| | Limestone. | Light Lime. | Heavy Lime. | Grappiers Cement. |
|---|---|---|---|---|
| Insoluble residue, . . | .. | ·15 | ·60 | 1·10 |
| Silica, . . . | 10·25 | 13·45 | 15·10 | 19·40 |
| Alumina, . . . | ·82 | 2·35 | 2·80 | 4·31 |
| Ferric oxide, . . | ·58 | 1·50 | 1·80 | 2·30 |
| Lime, . . . | 48·35 | 67·40 | 66·40 | 64·00 |
| Magnesia, . . | ·60 | ·90 | ·87 | ·86 |
| Sulphuric acid (SO₃), . | ·17 | 1·00 | ·96 | ·75 |
| Loss on Ignition, . | 39·20 | 13·20 | 11·45 | 7·25 |
| | 99·97 | 99·95 | 99·98 | 99·97 |

**Hydrated Lime in the United States of America.**—The hydraulic limes have not been greatly used in the United States, preference having been given to cement which, until recently, was obtained by calcining and grinding the natural cement rocks occurring so largely in many of the States, or by imported Portland. Since the introduction of the Portland cement industry, and its continued expansion, the imports have almost entirely ceased, while the use of the natural cements has steadily declined. Lime, other than hydraulic, has been placed upon the market in the state of hydrate by many manufacturers, and is finding increasing favour for purposes of construction. It is also employed as an addition to Portland cement mortar to increase its density and plasticity.

The process of hydration is conducted in machines called hydrators, each being capable of dealing with large quantities; some of them work continuously, others intermittently. In some types the lime may be treated direct from the kilns, without breaking or crushing, but, generally, it is crushed sufficiently fine to pass a sieve of ¼ inch mesh, or even finer than this. Care has to be taken to regulate the supply of water, which must be absolutely uniform for a given weight of lime and in greater quantity than theory requires, to allow for loss by evaporation, while it is necessary that the water should be brought in contact with every particle of lime. If the operation has been carefully conducted, the lime leaves the hydrator as a dry powder, from which any unburned or unslaked portions are removed by an air separator. The finished product is conveyed to silos, closed to the admission of air, from which it is drawn, weighed, and packed by automatic machines. Hydrated lime, as a marketed product, can be obtained in this country, but it has not yet been used for purposes of construction. Hydrators have recently come into use in some of the French hydraulic lime works.

The **Standard Specification of the American Society for Testing Materials** requires, as regards fineness, a residue not exceeding 5 per cent. on a sieve of 10,000 meshes, and not exceeding 0·5 per cent. on one of 900 meshes per square inch. The test for perfect hydration is made by mixing equal quantities by weight of lime and Portland cement, and gauging the mixture to a workable consistency. Of this, a pat or cake of about 3 inches diameter, ½ inch thick at the centre, and drawn down to a thin edge, is formed on a glass plate, allowed to remain in air for 24 hours, and then exposed for 5 hours in a loosely covered vessel to the action of steam given off by boiling water. At the end of this time, it should show no signs of cracking, warping, or disintegration. It is obvious that the cement used must, itself without admixture, be capable of complying with the test. This specification divides limes into four classes, according to their chemical composition—viz., high calcium, calcium, high magnesian, and magnesian. As kiln products into selected lumps, free from under-burned, ashes, and any foreign matter, and into the whole product, as drawn from the kiln, well burned. The chemical composition of each class is given in the following table. Hydrated limes take the same class as the lime from which they were prepared :--

ORDINARY LIME.

|  | High Calcium. | | Calcium. | |
| --- | --- | --- | --- | --- |
|  | Selected Minimum. | Whole Product of Kiln. Maximum. | Selected. | Whole Product of Kiln. |
| Lime, . . . . | 90 | 90 | 85 to 90 | 85 to 90 |
| Lime and magnesia, . | 90 | 85 | 90 | 85 |
| Silica, alumina, oxide of iron—maximum, . . | 5 | 7·5 | 5 | 7·5 |
| Carbon dioxide—maximum, | 3 | 5 | 3 | 5 |

MAGNESIAN LIME.

|  | High Magnesian. | | Magnesian. | |
| --- | --- | --- | --- | --- |
|  | Selected. Minimum. | Whole Product of Kiln. Minimum. | Selected. | Whole Product of Kiln. |
| Magnesia, . . . | 25 | 25 | 10 to 25 | 10 to 25 |
| Magnesia and lime, . . | 90 | 85 | 90 | 85 |
| Silica, alumina, oxide of iron—maximum, . . | 5 | 7·5 | 5 | 7·5 |
| Carbon dioxide—maximum, | 3 | 5 | 3 | 5 |

## CHAPTER IV.

## RETROSPECTIVE AND HISTORICAL REVIEW OF THE CEMENT INDUSTRY.

CONTENTS.—Smeaton's Discoveries—Practical Experiments—Cause of Hydraulicity—Use of Trass and Pozzolana—Composition of Mortars—Parker's Patents—Pasley's Tests—French and English Quick-setting Cements—Rosendale and American Natural Cements—Vicat's Artificial Lime—Frost's Patents—Early Cement Works.

**Smeaton's Discoveries.**—As we have stated in our opening chapter, the investigations of Smeaton undoubtedly paved the way for all the modern improvements in the treatment of limes and cements, and led to the overthrow of theories and prejudices which were as old as civilisation itself.

The discoveries of Smeaton, though they took place about 1756, were not published until many years later. In fact, it was not until 1791 that he described his experiments, in the third chapter of Book IV. of his "Narrative of the Building, etc., of the Eddystone Lighthouse."

Smeaton tells us that, having been taught a simple method of analysis by Mr. Cookworthy (to whom, by-the-bye, we owe the first use of kaolin in this country, discovered by him in Cornwall, and with which he subsequently produced the highly-prized porcelain of Plymouth and Bristol), he tested many varieties of lime, and soon found that the "acquisition of hardness under water did not depend upon the hardness of the stone (from which the lime was made), inasmuch as chalk lime appeared to be as good as that burnt from Plymouth marble, and that Aberthaw lime was greatly superior to either for aquatic buildings, though scarcely so hard as Plymouth marble."

**Smeaton's Practical Experiments.**—Till this point Smeaton had been guided by the experience of the past, for all writers on building, from Vitruvius to Belidor, had maintained this theory—viz., that lime burnt from dense, hard stone made the hardest mortar. But Smeaton's practical tests upset all these traditions, and he sought for some better explanation. He goes on to say, "I was very desirous to get some light into some of the sensible qualities that might probably occasion the difference, or at least be a mark of distinction." He then proceeds as follows :—

"Perhaps nothing will better show that the qualities of lime for water mortar do not depend on hardness or colour than a comparison of the white

lias of Somersetshire (which, though approaching to a flinty hardness, has yet a chalky appearance) with what is called near Lewes in Sussex the " clunch lime " ; a kind of lime in great repute there for water works, and indeed deservedly so.  This is no other than a species of chalk, not found like the lias in thin strata, but in thick masses as chalk generally is ; it is considerably harder than common chalk, but yet of the lowest degree of what may be denominated a stony hardness ; it is heavier than common chalk, and not near so white, inclining towards a yellowish ash colour. This stone when analysed is found to contain $\frac{3}{16}$ part of its weight of yellowish clay, with a small quantity of sand seemingly of the crystal kind, not quite transparent, but intermixed with red spots."

**Hydraulicity depends on Presence of Clay.**—" Hence the fitness of lime for water building seems neither to depend upon the hardness of the stone, the thickness of the stratum, nor the bed or matrix in which it is found, nor merely on the quantity of clay it contains, but, in burning and falling down into a powder of a buff-coloured tinge, and in containing a considerable quantity of clay, I have found all the water limes to agree.  Of this kind I esteem the lime from Dorking in Surrey to be ; which is brought to London under the idea of its being burnt from a stone,* and in consequence of that, of its being stronger than the chalk lime in common use there ; though in fact it is chalk, and not much harder than common chalk, it contains $\frac{1}{17}$ part of light coloured clay of a yellowish tinge."

**Colour not of Itself a Sufficient Indication.**—" There is in Lancashire a lime famous for water building called Sutton lime ; I have lately had an opportunity by favour of John Gilbert, Esq., to get a specimen of the stone in its natural state.  I had long since seen it in the Duke of Bridgewater's works, both in the burnt stone and slaked, made up for use and in the water I observed that it agreed with the lias in being of the buff cast.  The stone itself is of a deep brown colour, and the piece I·have is from a stratum about 3 inches thick, with a white clayey coat on each side.  The goodness of the quality as water lime does not, therefore, consist in the colour before it is burnt ; for we have already seen blue, whitish, and now brown, to be good for that purpose, but they all agree in the colour or hue after they are burnt and quenched ; and having analysed the Sutton limestone I find it to contain not only near $\frac{3}{16}$ part of the original weight of the stone, of brown or red clay, but also $\frac{1}{43}$ of fine brown sand, so that in reality I have seen no lime yet, proved to be good for water building, but what on examination of the stone contained clay ; and though I am very far from laying this down as an absolute criterion, yet I have never found any limestone containing clay in a considerable quantity but what was good for water building, and limes of this kind all agreed in one more property, that of being of a dead frosted surface on breaking, without much appearance of shining particles."

* *Dorking Stone Lime,* p. 12.

**Use of Trass and Pozzolana.**—In the same spirit of painstaking research Smeaton experimented with mixtures of lime with trass and pozzolana, which substances were known at that day to impart to fat limes hydraulic properties. For reasons, which he explains, he rejected the former and employed a mixture of blue lias lime from Watchet and pozzolana in equal parts, as this was, he conceived, the best water cement that could possibly be made. He likewise tried many other substances mixed with lime, such as the scales from a smith's forge and calcined iron ore.

The lime of Watchet, which he had found to be identical with that of Aberthaw (the beds being merely intersected by the estuary of the Severn), he caused to be slaked on the spot with just sufficient water to enable it to fall down to a fine powder, and this slaked lime was then packed in water-tight casks and sent to Plymouth, whence it was conveyed to the Eddystone rock for use as required.

**The Varieties of Mortars used by Smeaton.**—Smeaton gives an interesting table showing the composition of the various kinds of mortar he employed, as also the cost of each :—

| No. | Name of Mortar. | Winchester bushels by stricken measure of | | | No. of cubic feet. | Expense per cubic foot. |
| | | Slaked Lime Powder. | Pozzo- lana. | Common Sand. | | |
|---|---|---|---|---|---|---|
| | | | | | | s. d. |
| 1 | Eddystone mortar, . . | 2 | 2 | .. | 2·32 | 3 8 |
| 2 | Stone mortar, . . . | 2 | 1 | 1 | 2·68 | 2 1¼ |
| 3 | ,, 2nd sort, . | 2 | 1 | 2 | 3·57 | 1 7½ |
| 4 | Face mortar, . . . | 2 | 1 | 3 | 4·67 | 1 4 |
| 5 | ,, 2nd sort, . | 2 | ½ | 3 | 4·17 | 1 1 |
| 6 | Backing mortar, . . . | 2 | ¼ | 3 | 4·04 | 0 11 |

Smeaton is said by General Pasley,* in his well-known work, to which we shall often refer, to have been the first English engineer to use pozzolana, which he read of in the works of Belidor, but for want of chemical knowledge Smeaton failed to appreciate the full significance of the facts that he had observed.

**Parker's Patent in 1791.**—Within a very few years of the publication of Smeaton's work we find the record of Parker's invention of the cement made from " certain stones or argillaceous productions." His name, indeed, first appears in the " Patent Library Index " in 1791, when James Parker, of Christ Church, in the County of Surrey, claims, in Patent No. 1,806, the sole right to employ " a certain material never before made use of "

* *Observations on Limes, Calcareous Cements, Mortars, Stuccos, and Concrete,* by C. W. Pasley, C.B. London, 1838. 8vo.

for " burning bricks and tiles, and calcining chalk, earth, stone, and lime-stone." This he discloses in his specification to be " peat or bog," which was to be interstratified in the kiln with the material to be calcined. As an indication of the quantity needed, he states : " as, for instance, if it requires 36 bushels of coal to burn 220 bushels of lime, the same may be burnt or calcined with 220 bushels of peat with the addition of 3 bushels of coals."

**Parker's Second Patent for Cement.**—We cannot say with certainty, though it seems probable, that this was the same James Parker who on 28th June, 1796, claims in Patent No. 2,120 the invention of " A certain Cement or Terras (trass) to be Used in Aquatic and other Buildings, and Stucco Work." He describes his process as follows :—" The principle and nature of the said invention consists in reducing to powder certain stones or argillaceous productions, called noddles (sic) of clay, and using that powder with water so as to form a water (mortar ?) or cement stronger and harder than any mortar or cement now prepared by artificial means. I do not know of any precise generical term for these noddles of clay ; but I mean by them certain stones of clay or concretions of clay, containing veins of calcareous matter, having frequently but not always water in the centre, the cavity of which is covered with small crystals of the above calcareous matter, and the noddles agreeing very nearly in colour with the colour of the bed of clay in or near which they are found. These noddles, on being burnt with a heat stronger than that used for burning lime, generally assume a brown appearance and are little softened, and when so burnt and softened become warm (but do not slack) by having water thrown upon them, and being reduced to powder after burning, and being mixed with water just sufficient to make them into a paste, become indurated in water in the space of an hour, or thereabouts. Any argillaceous stone, then, corre-sponding with this description, whether known by the name of noddles of clay, or any other name, is the sort and kind only that I mean to appropriate to my own use in the fermentation (formation ?) of my cement."

**The Preparation of the Cement.**—" The manner in which I prepare and compose this cement is as follows, viz. :—The stones of clay or noddles of clay are first broken into small fragments, then burnt in a kiln or furnace (as lime is commonly burnt) with a heat nearly sufficient to vitrify them, then reduced to a powder by any mechanical or other operation, and the powder so obtained is the basis of the cement."

**Mode of Using the Cement.**—" To compose the cement in the best and most advantageous manner, I take two measures of water and five measures of the powder thus described ; then I add the powder to the water, or the water to the powder, taking care to stir and beat them during the whole time of intermixture ; the cement is then made, and will set or become in-durated either in ten or twenty minutes after the operation has ceased, either in or out of water.

" But although I have described what I consider as the best proportions for the composition of the cement, it is expressly to be understood that these and all other proportions are to be included within the meaning and purposes of this specification, but that no other proportions will produce so strong a cement in so short a time as those I have here pointed out ; and also that I occasionally burn, and grind, and mix the powder before described with lime and stones, clay, sand, or calcined earth in such proportions as may be necessary and useful for the purpose that the cement is intended to be applied to, always observing the less water is used the better, and the sooner the mortar or cement is used after being made the stronger and the more durable it will be."

**Parker's Cement termed Roman Cement.**—In the above patent Parker is described as of " Northfleet, in the County of Kent, gentleman." According to Pasley, it was not until some years later that he applied to the new material the misleading name of " Roman " cement. He shortly afterwards traded in partnership with Mr. Wyatt, and used the stones found at Sheppey in the manufacture of the cement, which soon became known under the name of " Parker's cement." A certain Mr. Samuel Wyatt had previously acquired experience in the use of materials for stucco, and his name is frequently mentioned by Dr. Higgins in his work on Cements.*

**Derivation of the Septaria.**—The pebbles used for cement-making were obtained at various places on the Kentish coast, those from Minster Manor and Whitstable being apparently in the best repute. It was not until very much later that Frost made use of the Harwich dredged stone, after which time it was customary to employ a mixture of Harwich and Sheppey stones in equal proportions to burn the best Roman cement, though Pasley tells us that, about 1836, in the Government dockyard at Sheerness, they used one part of Sheppey to three parts of Harwich cement stone. The makers of artificial cements about this period sold the cement made from natural stone at a much higher price than that made from a mixture of chalk and clay.

**Pasley's Tests of Cements in 1836.**—The following table compiled from Pasley's book is valuable as showing the comparative merits of the chief cements in use at the time he wrote (1836). All the specimens were tested neat:

| Sort of Cement Used. | Age in Days. | Total Tensile Strength in Pounds. | Lbs. per Sq. In. |
| --- | --- | --- | --- |
| Pasley's artificial cement, . . | 11 | 1,395 | 34·9 |
| Frost's artificial cement, . . | 11 | 705 | 17·6 |
| Francis (Natural), . . | 11 | 1,223 | 30·6 |
| Sheerness (Natural), . . | $\left\{ \begin{matrix} 10 \\ 12 \end{matrix} \right\}$ | 1,220 | 30·5 |

* *Experiments and Observations made with the View of improving the Art of Composing and Applying Calcareous Cements*, by Brindley Higgins, M.D.  London, 1780.  8vo.

**French Quick-Setting Cements.**—The quick-setting cements of the Roman type, made in accordance with Parker's patent, had their counterpart in France, for about 1796 a French military engineer, named Lesage, drew attention to the eminently hydraulic properties of the pebbles of Boulogne-sur-Mer, and from these he produced a material which he called "plaster-cement," though this substance was quite distinct from the compounds of the calcic sulphate series.

Another quick-setting cement, which obtained a wide reputation on the Continent, was that of Pouilly, discovered by Mons. Lacordaire in 1829. Four years later, in 1831, Mons. H. Gariel first introduced the well-known cement of Vassy. Another cement of a similar character, which has been much used in France, is made from stone dug near Grenoble at Porte-de-France.

**Analyses of French and English Cement-Stones.**—The composition of all these raw materials is very similar, as will be seen by the following set of analyses, made in Paris, at the École des Mines :—

|  | English Roman. | Boulogne. | Vassy. | Pouilly |
|---|---|---|---|---|
| Silica, . . . . . | 15·42 | 14·27 | 16·0 | 17·14 |
| Alumina, . . . . . | 5·63 | 5·81 | 6·50 | 6·87 |
| Iron, . . . . . | 6·81 | 5·97 | 8·60 | 4·83 |
| Magnesia, . . . . | 0·83 | 0·67 | 1·50 | 3·39 |
| Manganese, . . . | 0·54 | 0·83 | .. | 0·17 |
| Lime, . . . . . | 45·12 | 46·20 | 46·80 | 47·35 |
| Loss on calcination, moisture, and carbonic acid, . . . . | 25·65 | 26·25 | 20·60 | 20·25 |
|  | 100·00 | 100·00 | 100·00 | 100·00 |

The Vassy cement, which is very dark in colour, is the richest in iron, and sets when freshly burned with great rapidity. The cement-stone of Grenoble is very similar in its composition to the above, but contains rather less clay. In France, the quick-setting cements are, as a rule, ground under edge-runners, and passed through copper wire sieves of 324 meshes per square centimetre (2,090 per square inch).

**Magnesian Cements of America.**—Of the so-called natural cements of America, which, before the introduction of the manufacture of Portland cement, had obtained such a widespread employment in every kind of engineering work in that country, many partake somewhat of the nature of Roman cement, and may be mainly considered, according to one of the most recent American writers on this subject—Cummings [*]—under two heads, as disilicates, or trisilicates. The former class includes all rock

[*] *American Cements*, by Uriah Cummings.  Boston, 1898.

cements composed of disilicates of lime and alumina, and the latter the trisilicates of lime, magnesia, and alumina. It is stated that in 1894 the annual production of American rock cements amounted to 7,595,676 barrels, and the proportions of these two classes were as follows :—

1. Disilicates,    .    .    .    .    .    2,557,464 barrels.
2. Trisilicates,   .    .    .    .    .    5,038,212     ,,

It must be understood that the above classification is somewhat arbitrary, as many of the so-called disilicates will be found to include a small percentage of the tri- and also of a mono-silicate. The position of a cement in the above classification depends, therefore, on the particular form of silicates indicated by its predominance. The disilicates are, as a rule, of the Portland cement type, and are frequently calcined at a white heat; the trisilicates are fired at a lower temperature, and are more of the nature of Roman cement. As a type of the trisilicate cements, we may describe the famous Rosendale cement, named after the town of Rosendale, where it was originally discovered, and largely used in the construction of the old Delaware and Hudson canal.

**Raw Materials for American Cements.**—The formation which furnishes the raw materials for this cement is an argillaceous magnesian limestone, which extends along the whole of the Appalachian range, and was said to yield formerly three-fourths of the hydraulic cement produced in the United States. The workable beds are seventeen in number, and the method of manufacture is as follows :—

The limestone, which is blasted by black powder, is conveyed to the kilns on trucks running along the base of the quarry. The stone is arranged in the kilns in layers interstratified with small coal. The kilns are cylindrical in form, but have a conical contraction at the bottom. They are worked continuously, portions of the charge being withdrawn every twelve hours. The underburnt lumps are passed a second time through the kiln; the fully calcined stone is conveyed in elevators to the top of the mill. Here it is first broken to a small gauge (size of hazel-nut) in a cracker, which is a machine somewhat on the principle of the coffee-mill. Each cracker will prepare from 250 to 300 barrels of cement per diem for the mills.

**Grinding of the Calcined Cement.**—The mill-stones are only 3 feet in diameter, but they grind the cement so fine that from 93 to 95 per cent. will pass a 50 × 50 mesh sieve. These mills differ from those in use in this country for cement-grinding, in that, what is termed in England the "runner," or the upper stone, is fixed and the lower one revolves. The ground cement is conveyed by "creepers" to the packing room, where it is put up in paper-lined casks, and is then ready for use.

**Yield and Composition of the Beds.**—Each cubic yard of cement stone yields about 2,700 lbs. of finished cement. The various beds of stone fluctuate

very considerably in their composition, and the preparation of the cement and the mixture of the raw materials from the different levels is a matter of great nicety. During the manufacture the cement is carefully tested, four briquettes being made every hour. The pattern used for the moulds differs from that in common use in Europe.

**General Gillmore's Tests.**—General Gillmore, whose work on cements * may be consulted with advantage respecting the manufacture and employ-ment of these materials, puts the crushing strength of the neat cement at 546 lbs. per square inch in seven days, and 2,015 lbs. per square inch in thirty days. The tensile strength of the neat cement is 104 lbs. per square inch in seven days, and 134 lbs. per square inch in thirty days. With an equal amount of sand the tensile strength in thirty days is 102 lbs. per square inch.

**Louisville Cement.**—Cement rock was discovered at Louisville, Kentucky, in the year 1829, and, having been used for the Louisville and Portland Canal, it was found to be of good quality. The district, owing to the con-venience of transport afforded by the Ohio River, speedily became the centre of an important industry, second only to that of the Rosendale district. The Louisville cement contains less magnesia than the Rosendale, for while the magnesia in the former may average from 9 to 10 per cent., the magnesia found in the Rosendale cement may reach as much as 18 per cent. The stone from which the cement is made is peculiar to a small area, only a few miles wide, extending north of the Ohio River about 15 miles. No admixture of various strata is necessary in making this cement, the formation being uniform in all essential characteristics. The stone, much of which is mined in open quarries, is broken into pieces of three uniform sizes by crushers and fed into the kilns, which are 45 feet high and 16 feet in diameter. These kilns are constructed of iron, lined with firebrick; the stone is burnt with coal loaded into the kiln in alternate layers with the stone. The firing operations are continuous, and the kilns, which are lighted in the spring, are only extinguished when the operations cease for the winter. The calcined stone is withdrawn from openings near the base of the kiln and fed into the coarse crushers, and all imperfectly burned material is picked out by hand. From the coarse crushers the stone passes into the fine crushers, and it is ultimately ground to powder between emery mill-stones.

Extensive works for the production of rock cement exist also at Mil-waukee, Buffalo, La Salle, Utica, Akron, in various parts of the Lehigh Valley, and in Georgia.

While certain of the rock cements are calcined at a relatively low tem-perature, others are burnt at a heat which approaches that required to produce Portland cement clinker, and the colour varies between very wide limits.

* *Practical Treatise on Limes, Hydraulic Cements, and Mortars,* by Q. A. Gillmore, A.M.  New York, 1874.

**Natural Cements now held in less Esteem in America.**—Owing to the great impetus given in recent years to the manufacture of Portland cement in the United States, the production of natural cements would appear to have fallen off. We have dealt with the analysis of the American natural cements at p. 57.

**Early Cement Patents in England.**—The records of the Patent Office of this country show us that prior to the advent of Parker some eighteen inventors had busied themselves with processes for burning lime, for the manufacture of "tarrass," or pozzolana, for a composition or cement called "Pietra Cotta," and for sundry descriptions of mastic, mortar, and stucco. Among these we find the "water cement or stucco" described in the work already mentioned by Dr. B. Higgins. This patent is No. 1,207, and is dated January 8, 1777.

From the date of Parker's second patent in 1796 to that of James Frost's specification in 1822, the Patent Index likewise includes eighteen patents, one of the most notable of which was that granted to St. Leger in 1818.

**St. Leger's Patent in 1818.**—St. Leger was probably the concessionaire of Vicat, a French engineer, whose experiments with limes and cements are justly famous, and his work may here receive passing notice. Omitting the investigations of Loriot, published in 1774, those of De La Faye, said to have been made known in 1777, and the artificial stone of Fleuret, described in his book dated 1807, all of which are duly recorded by Pasley, we come to the publication of Vicat in 1818.* It will be impossible here to do more than refer most briefly to his treatise, but as his later work in 1828 † has been ably translated by Captain Smith, and as General Pasley alludes at considerable length to his investigations in the appendix to his *Observations on Lime, Calcareous Cements, etc.*, we need not dwell on them very fully.

**Vicat's Artificial Lime.**—Vicat, who appears to have been the first to apply the term "hydraulic" to limes for use in water, prepared mixtures of pure lime and clay, and calcined the resulting material in kilns. He employed, originally, slaked lime powder, together with 20 per cent. of clay, but in his second treatise he describes a plan of grinding chalk along with the requisite proportion of clay. His process was actually carried out at Meudon by Messrs. Bryan and St. Leger, who used the chalk found in the vicinity, and the plastic clay of Vaugirard. They ground together in a wash-mill four measures of chalk and one of clay with a considerable quantity of water, and the fluid slip was then run into reservoirs to dry. When stiff enough the pasty mass was moulded into blocks and burnt in kilns, inter-stratified with small coal and coke. This plan of making an artificial lime

* *Recherches Expérimentales sur les Chaux de Construction, les Bétons et les Mortiers Ordinaires*, par L. J. Vicat. Paris, 1818. 4to.

† *Résumé des connaissances positives actuelles sur les qualités, le choix et la convenance réciproque des matériaux propres à la fabrication des Mortiers et Ciments Calcaires, etc.*, par L. J. Vicat. Paris, 1828.

was still practised at Meudon when one of the authors visited the works in 1878.

Vicat shares with Dr. John of Berlin the honour of having explained the importance of the presence of clay in combination with lime, on scientific grounds, though De Saussure first pointed out that hydraulicity depended solely on the presence of clay, and Descotils in 1813 observed that this phenomenon was due to the existence of a large quantity of siliceous matter disseminated through the mass in very fine particles. Dr. John's treatise was published in 1818. Smeaton, as we have stated, anticipated by many years these discoveries, though he failed to turn them to practical account.

**Specification of St. Leger's Patent.**—Doubtless it was a process similar to the above which was, as we have seen, patented in this country in 1818 (No. 4,262). M. Maurice St. Leger describes himself in the specification as of St. Giles, Camberwell, in the County of Surrey. The patent is for " an improved method of making lime " out of a fat or pure carbonate of lime by the addition to the same of " clay or any substance containing alumine and silex." The general proportion named by St. Leger is " from 1 to 20 measures, or given quantities of clay or other substance containing alumine and silex, to every 100 measures or given quantities of chalk, stone, or other substance, or of lime." It does not appear that St. Leger worked the patent in England.

**Frost's Patent for British Cement in 1822.**—On the 11th of June, 1822 (No. 4,679), James Frost, of Finchley, in the County of Middlesex, Builder, specifies " a new cement or artificial stone," which is made as follows :— " I select such limestones or marls, or magnesian limestones or marls as are entirely or nearly free from any mixture of alumina or argillaceous earth, and contain from 9 to 40 per cent. of siliceous earth or silica, or combinations of silica and oxides of iron, the silica being in excess and in a finely-divided state, and break such selected materials into small pieces, which are then calcined in a kiln, in the manner calcareous substances usually are, until all carbonic acid be expelled, and until it be found on trial of a small portion of such calcined materials that it will not, when cool, slack or fall when wetted with water. The calcined material is to be ground to a fine powder by any machinery fit for reducing dry substances to that state, and the powder is the material for making the cement or artificial stone, and must be kept in dry packages for use. When used it is to be mixed with water, and tempered to the consistency of common mortar : it should be mixed in small quantities and applied instantly to its intended purpose, as it will set in a few minutes to resist the impression of the finger and gradually harden to a stony body. For many purposes a quantity of clean siliceous sand may be advantageously incorporated with it when it is tempered for use. The cement will be lighter or darker in colour, as there is a lesser or greater quantity of oxide of iron in the selected materials; the lighter

colour will be found best adapted to dry, and the darker colour to wet situations.

" I declare that my invention is for making a cement or artificial stone from siliceous limestones or marls in the manner hereinbefore described, and that I shall call it by the name of British cement."

There are some singular blunders in this specification which prove conclusively that Frost had a poor grasp of chemistry. Thus he proposes to use limestone or marl " free from any mixture of alumina," but containing " from 9 to 40 per cent. of silica," which would be pure sand, and would inevitably yield a compound devoid of cementitious properties.

**Frost's Second Patent.**—In 1823 (No. 4,772), Mr. Frost describes a process of " calcining and preparing calcarious (sic) and other substances for the purpose of forming cements," with which object he used a kiln of special construction, in which the material was permitted to cool very slowly; this is an invention of no importance, and it was probably founded on a misconception.

**Frost as a Cement-maker.**—Very shortly afterwards, in 1825, Frost established himself in cement works at Swanscombe, on the Thames, and became the first maker of artificial cement in the London district. Frost's business was carried on by him until 1832 or 1833, when his interest was acquired by Mr. John Bazley White, Senr., who at first was the partner of Mr. Francis. Pasley tells us that Messrs. Francis, White & Francis " were in the habit of selling their artificial cement at one shilling per bushel at the same time that they sold their natural cement for eighteen pence."

Mr. Frost, when he had disposed of his business, retired to America, and we can find no further records of his career. His works were carried on by Messrs. Francis & White in partnership until January 1, 1837, when they were made over entirely to Messrs. White & Son, who had also works at Millbank. Mr. Francis, who traded as Messrs. Francis & Sons, founded the well-known works at Nine Elms, Vauxhall.

In strict historical sequence we should before this have referred to Aspdin and his invention of Portland cement, but this may form the subject of a special chapter.

# CHAPTER V.

## THE EARLY DAYS OF PORTLAND CEMENT.

**Portland Cement first made by Aspdin.**—The somewhat misleading name of
" Portland " cement was given to the artificial compound of lime and clay,
prepared by Mr. Joseph Aspdin, a Leeds bricklayer. He chose this name in
consequence of its fancied resemblance in point of colour and texture to the
oolitic limestone of the island of Portland, well known and in great favour
in this country as a building stone.

**Aspdin's Specification.**—Aspdin's specification, No. 5,022, is dated
October 21, 1824, and is for " An Improvement in the Modes of Producing
an Artificial Stone," which invention he thus describes :—" My method of
making a cement or artificial stone for stuccoing buildings, water works,
cisterns, or any other purpose to which it may be applicable (and which
I call Portland cement) is as follows :—I take a specific quantity of limestone,
such as that generally used for making or repairing roads, after it is reduced
to a puddle or powder ; but if I cannot procure a sufficient quantity of the
above from the roads, I obtain the limestone itself and I cause the puddle
or powder, or the limestone as the case may be, to be calcined. I then take
a specific quantity of argillaceous earth or clay, and mix them with water
to a state approaching impalpability, either by manuel (sic) labour or
machinery. After this proceeding I put the above mixture into a slip pan
for evaporation, either by the heat of the sun or by submitting it to the action
of fire or steam conveyed in flues or pipes under or near the pan, until the
water is entirely evaporated. Then I break the said mixture into suitable
lumps, and calcine them in a furnace similar to a lime kiln till the carbonic
acid is entirely expelled. The mixture so calcined is to be ground, beat,
or rolled to a fine powder, and is then in a fit state for making cement or
artificial stone. This powder is to be mixed with a sufficient quantity of
water to bring it into the consistency of mortar, and thus applied to the
purposes wanted."

**Aspdin's Second Patent.**—Aspdin, whose name, by-the-bye, in the "Alphabetical Index of Patentees" is mis-spelled "Apsdin," obtained protection in the following year, 1825, under date of June 7 (No. 5,180), for "a Method of Making Lime." In order to effect this, he collected the road scrapings from roads repaired with limestone ; these he dried, either by natural or artificial heat, and they were subsequently "removed to a furnace or kiln to burn with coal, coke, or wood." The product was then ready either for "building, or liming land."

**Aspdin's Process** differs from that used subsequently. It is difficult to recognise in this description a process likely to result in the formation of a cement of the present Portland type. It must be remembered, however, that Aspdin had a hard mountain limestone to deal with, and that probably the most easy way to obtain this material in a state of fine subdivision, in order to mix it with clay, was to calcine it. It could then readily be slaked and reduced to powder. The next step was to temper it with the requisite amount of clay, and finally the mixture was submitted to a second process of calcination. This double-kilning would, where fuel was relatively cheap, entail but little more cost and perhaps less labour than first grinding the limestone to fine powder under mill-stones and then mixing it with the clay, as is now done in the dry process of manufacturing Portland. Moreover, by the slaking action, the lime is obtained in an extremely fine state of subdivision, and, therefore, in a condition peculiarly well adapted for intimate admixture with the clay.

**Defects in Aspdin's Specification.**—Aspdin fails to point out the exact amount of clay needed—rather an important matter in a specification, one would think—and he omits to state that the firing must be carried on until incipient vitrification is attained. These omissions might by some be regarded as casting doubts upon the authenticity of his discovery of Portland in 1824, but it is a well-known fact that he had a manufactory of Portland cement for many years at Wakefield, which was established in 1825, and which is still in existence, though no longer on the original site. Moreover, his son, William Aspdin, was, as we shall see, one of the early cement manufacturers in the Thames district.

**Proposals to make Cements from Artificial Mixtures.**—On searching the Patent Office records it is found (as we have already mentioned) that other inventors had attempted to produce cements from mixtures of lime and clay, and Pasley has, in his important work on cements, previously noticed, recorded a long series of patient investigations and experiments, having for their object the formation of an artificial cement capable of giving like results to those obtained from the natural cements, made from the septaria of the London clay, and the nodules of argillaceous limestones found in the Isle of Sheppey.

**Roman and Quick-setting Cements.**—In our previous chapter we have

given a brief account of these materials, and of the artificial hydraulic lime of Meudon, the invention of Vicat. Cements of this type were, in the early years of the previous century, in very general use in this country, and many attempts were made by inventors to obtain a cheaper source of supply. It was clearly the search after such substitutes for the natural cement stone which led to the discovery of Portland cement, and though this latter material has now very largely displaced the quick-setting cements of former days, there are no doubt many purposes for which Roman cement can be used with advantage, and this cement is still in frequent demand.

**Early History of Portland Cement by Pasley.**—We know but little of the early history of Portland cement. General Pasley, in the preface of the second edition of his work, dated August, 1847, states:—" At present there are three manufactories of artificial cements in England, which have all been used more or less extensively in works of importance, and have given satisfaction, viz.:—First, that of Messrs. John B. White & Sons, in the Parish of Swanscombe, Kent, the present proprietors of Mr. Frost's Works, who, after gradually relinquishing the objectionable parts of his process, have succeeded in making a good artificial cement, which they call their Portland cement, by a mixture of chalk found on their own premises with the blue clay of the Medway; secondly, that of Messrs. Evans & Nicholson, of Manchester, who make an artificial cement, which has been called the patent lithic cement, with the very same ingredients, and in the same proportions, nearly, that were used in the author's experiments, but the most important of which is obtained in a roundabout manner from the residual matters or waste of certain chemical works, instead of working with natural substances; thirdly, that of Mr. Richard Greaves, of Stratford-on-Avon, who makes a powerful water cement, which he calls blue lias cement, by mixing a proportion of indurated clay or shale with the excellent blue lias lime of that neighbourhood, both of which are found in the same quarries; the former being previously broken and ground, and the latter burned and slaked, which is absolutely necessary in making an artificial cement from any of the hard limestones."

**Pasley's Letter to Dr. Garthe.**—This account of the Portland cement industry was, however, incorrect, for we find in a letter published in *Dingler's Polytechnisches Journal*,[*] written by Pasley to Dr. Garthe, of Cologne, and dated March 3, 1852, the following additional information on the subject:—
" I am much flattered by the favourable opinion you express concerning my work on cement. As shortly after my promotion to the rank of Major-General I ceased to occupy the post of Inspector of the Royal Engineers' School at Chatham, and had, therefore, neither assistants, materials, nor appliances at my disposal, I was no longer in the position to prosecute researches of a similar nature to those formerly carried on by me, and which

* Vol. cxxiv., p. 27.

resulted in the discovery of an artificial compound but little inferior to the best natural cements.

"For several years past I paid no further attention to the subject until I learned that Portland cement was superior to Roman cement; and as it is the fashion in our country to disguise everything with some fantastic name or other, which, except in the case of chemical products, gives not the slightest clue to the composition of the article in question, I was astonished to discover that this Portland cement, the name of which would lead the foreigners visiting our great Industrial Exhibition of last year to believe very naturally, either that it was a cement found in the island of Portland, or that it was related in some way or other to Portland stone, was neither more nor less than my own artificial cement, compounded of chalk and clay.

"Messrs. Robins, Aspdin & Co. manufacture Portland cement* which appears to me to be just as good as, if not superior to, that of Messrs. White & Sons, although I never heard of it until I met Mr. Aspdin in the great Exhibition last year. I was present at all the experiments upon Portland cement mentioned in *The Builder* of the 27th September last. The results of the same are correctly reported, but several of them are rendered ambiguous for want of more complete particulars, or of the explanatory drawings relating to them."

**Becker's Book on Portland Cement in 1853.**—In a German work on Portland cement by Becker,* in which this letter is quoted, and which, we believe, was the first treatise in any language on this material, there is a footnote calling attention to the singular fact that, "although Joseph Aspdin, the inventor and patentee of Portland cement, established his manufactory at Wakefield in 1825, and his son, William Aspdin, founded his works at Northfleet, on the Thames, about 10 miles from Chatham, a few years later, at which latter place Sir C. W. Pasley was then residing, and although their Portland cement was already much employed on the Continent, as introduced in the first instance by Maude & Son, and subsequently by Robins, Aspdin & Co., whereas the cement of Messrs. White & Sons was not brought into the market until many years later (in 1845), Sir Charles Pasley only heard for the first time of the existence of Joseph Aspdin, the inventor of Portland cement, and of his manufactory (at Wakefield) in the great Exhibition of 1851."

**Aspdin, the Younger.**—Mr. Becker is, however, not quite correct in his facts, for young Aspdin did not go to Northfleet until 1848. It appears that he at first associated himself with Messrs. J. M. Maude, Son & Co., of Upper Ordnance Wharf, Rotherhithe, and from a circular issued by this firm in 1843 we learn the following particulars respecting their business, and relative to the cement industry at that date :—

**Circular by J. M. Maude, Son & Co.**—"The manufacture of this cement (patent Portland cement) has for many years been carried on by Mr. Aspdin at Wakefield, in which neighbourhood, as throughout the northern counties

* *Erfahrungen über den Portland Cement*, Berlin, 1853. 8vo.

of England, it has been successfully and extensively used; owing to the heavy charges attending its conveyance to the London market its consumption there has necessarily been limited, and although its superiority over other cements has never been contested by those who have been induced to give it a trial, the high price at which alone it could be supplied has hitherto proved a serious impediment to its more general introduction into the metropolis. Messrs. J. M. Maude, Son & Co. have now the satisfaction of announcing to the public that they have made arrangements with the son of the patentee for the purpose of carrying on the manufacture of this valuable cement at their extensive premises at Rotherhithe; and whilst they will thus be enabled to supply it at a considerably reduced price, they have also the satisfaction of stating that, in consequence of improvements introduced in the manufacture, it will be found, for the following reasons, infinitely superior to any cement that has hitherto been offered to the public :—

"(1) Its colour so closely resembles that of the stone from which it derives its name as scarcely to be distinguishable from it.

"(2) It requires neither painting nor colouring, is not subject to atmospheric influences, and will not, like other cements, vegetate, oxidate, or turn green, but will retain its original colour of Portland stone in all seasons and in all climates.

"(3) It is stronger in its cementitive qualities, harder, more durable, and will take more sand than any other cement now used."

After alluding to its value as a stucco and for paving purposes, the circular states—" It is manufactured of two qualities, and sold in casks of 5 bushels, each weighing about 4½ cwts. No. 1 at 3s. per bushel, or 20s. per cask, and No. 2 at 2s. per bushel, or 16s. 3d. per cask, 4s. 6d. each allowed for the casks, if returned in good condition." From the directions for its use we learn that the best quality was to be employed with four parts of sand.

**Early Tests of Portland Cement.**—Certain particulars are likewise given of some comparative trials of this Portland cement with Roman cement, which were conducted by Messrs. Grissell & Peto at the new Houses of Parliament in 1843, together with a letter from these eminent contractors, dated from York Road, Lambeth, 13th November, 1843, setting forth the fact that the experiments in question, which consisted of bricks stuck one on to another projecting from a wall, and of brick beams with bearings of 3 and of 5 feet, were made by their direction and under their own superintendence, and they add—" The results as shown by the above statement afford very satisfactory evidence of the superior qualities of your cement." They conclude that Portland with three parts of sand was more than double the strength of Roman cement with one part of sand, and that with Roman at 1s. 4d. and Portland at 2s. 3d. the bushel there was a saving of from 1½d. to 2d. per bushel of mortar in using Portland, owing to the increased volume of sand this latter cement would carry.

**Wylson on Portland Cement.**—It was just about this period that Portland began to make a London reputation, and in some articles on "Mortars and Cements" in *The Builder* in 1844, Mr. Wylson, speaking of these same experiments, says : "The deductions thence arrived at show an advantage on the side of the Portland cement, which speaks most strongly in its favour ; and which, judging by the authority from which these contrasts emanate, must be considered as at once authentic and conclusive, establishing this to be beyond all doubt superior to the Roman cement, whether as to strength, adhesion, or the capacity of receiving sand ; the latter of which properties it is shown to possess to such a degree as to render it actually cheaper than the Roman cement, whilst its other recommendations of beauty and the saving of colouring alone render it highly preferable."

**Early Advertisements relating to Portland Cement.**—Advertisements relating to this cement as made by Messrs. J. B. White & Sons appear for the first time in *The Builder* in October, 1845, and on the occasion of an accident to some stucco on a house in Cornhill, which had failed or " blown," in the following year, Messrs. Maude, Jones & Aspdin write under date of 3rd September, 1846, to deny that the cement in question was of their manufacture.

**Sir William Tite on Portland Cement.**—In May of this same year, Mr. W. Tite, the then Vice-President of the Institution of British Architects, spoke of Portland cement as " a good material if properly made and properly applied."

We have now reached the period when the railway fever set in, and the demand for cement stone. at Harwich became very extensive, indeed the stock of stone threatened to become exhausted. We read in December, 1846, " prices have in consequence risen 30 per cent., while the dredgers are reaping a proportionate benefit. It is calculated that £25,000 per annum are paid away in wages alone to workmen employed in this trade."

**Predicted Exhaustion of Natural Cement Stone.**—It must have been in the year 1845 or 1846 that Sir R. Peel announced in Parliament his intention of taxing the cement stone, fearing its exhaustion, and hoping thus to reserve a sufficient supply for the purpose of Government works. This fact we learn from a pamphlet issued by Messrs. Aspdin, Ord & Co. about 1854, who state also therein that, " As soon as Mr. Wm. Aspdin heard of this he addressed Sir Robert Peel upon the subject, and intimated to him that he need not be alarmed about the supply of " Roman cement," as an article, which far surpassed it, was extensively manufactured. To prove these remarks, Mr. Aspdin waited upon Sir R. Peel with samples, and obtained a reply to the effect that he was much satisfied with them, and with the explanation ; and in consequence the proposed tax was abandoned." In this pamphlet, which describes the firm as carrying on business at New Wharf, Abingdon Street, Westminster, and at Gateshead-on-Tyne, it is

stated that their total manufacturing powers were equal to 3,000 casks per week, and the price of the cement is quoted at 2s. per bushel. The results are given of several series of tests, and there is a challenge to rival manufacturers, dated December 16, 1852, to submit their cements to public tests, in accordance with which experiments were carried out at their wharf at Millbank on February 10, 1853.

**Portland Cement from Wakefield used in Thames Tunnel.**—From this same pamphlet we find that the Wakefield cement was largely used in the Thames Tunnel about 1828, although " at that time it cost 20s. to 22s. per cask, besides the carriage to London. Yet Sir I. Brunel decided (notwithstanding his ability to procure Roman at 12s. per cask delivered on the spot) to adopt Portland chiefly for his purpose, as its merits required no other recommendation than an impartial trial."

From this statement we may assume that the Thames Tunnel was the first engineering work of importance in which Portland cement was used, for there can be no doubt that in its early days it was mainly a stucco cement, and it was not until very much later that it acquired the confidence of the engineering profession.

**Accident at Euston Station in 1848.**—The year 1848 was in many ways a very eventful one in the history of Portland cement. On the last day of January a fatal accident occurred at Euston Station owing to the incautious use of Roman cement. A lofty wall supported on columns formed of brick on edge suddenly fell, causing the death of two workmen, and at the inquest which followed, and which attracted much attention, the question of the employment of cement was discussed at great length. Mr. Hardwick, the architect, expressed an opinion that the failure of the cement was due to its employment during the cold winter weather, and also to the great haste with which the work was run up. The columns in question were 20 feet high, 2 feet 2½ inches in diameter at the base, and 1 foot 10½ inches in diameter below the capital. Messrs. W. Cubitt & Co., the builders, stated that they could not assign a reason for the fall of the wall. On February 11, Mr. William Aspdin wrote from Northfleet and attributed the accident solely to the use of defective cement. We have here an intimation of Aspdin's removal from Rotherhithe.

**Experiments at Messrs. Grissell's Works in 1847.**—Later on in this same year, the results of some trials of Messrs. White's Portland cement are published in *The Builder*. These experiments had taken place at Messrs. Grissell's ironworks on December 10 and 31, 1847, and they furnished additional evidence of the superiority of Portland over Roman cement.

**Aspdin's Circular in 1848.**—The above trials and the publicity they obtained seem to have given considerable umbrage to Aspdin and his partners, for in the September following he published a letter as an advertisement in *The Builder*, in which he set forth, among other matters, that this cement

was first introduced by his father in 1813, and patented by him as " the Portland cement " in 1824, and that the original material is solely made by him. He quotes certain tests to show that he had obtained far better results than Messrs. White had done, and that he had used more sand. Thus he states that he has made blocks consisting of one part of cement to ten parts of sand, and he concludes by calling attention to a public trial of their cement which the firm were about to institute at their wharf at Great Scotland Yard.

**Experiments in 1848 at Messrs. Bramah's Works.**—These proposed experiments they advertised for some time, and they challenged all other cement makers to compete with them. The trial came off on the 18th September, and subsequently at Messrs. Bramah's works on the 26th, when some blocks were crushed by hydraulic pressure. We extract the following particulars from *The Builder* of September 30, 1848, as they show the quality of the cement at that period. The brick tests were of the usual character—viz., built out from the wall. In one case the beam consisted of 38 bricks joined with neat cement. With one part sand, 15 bricks were formed into a beam, a brick being added daily. Some brick beams were also tested, but the results are not very clear. Two large blocks of Portland stone, jointed together with cement, failed in the stone work. Some blocks of cement, 18 inches × 9½ inches × 9 inches, were then tried in a Bramah press, and stood 58¼ tons, when the press gave way. Roman cement failed under 22½ tons. A block of one part cement to one sand withstood 45 tons. On the 26th September some further tests were made with a better press at Messrs. Robinson & Sons, Pimlico, when the following results were obtained :—

" 1. One of the previous blocks, all cement and then thirty-five days old, bore a pressure of 68 tons, when it cracked at one angle, but ultimately bore 90 tons without any alteration.

" 2. An exactly similar block bore 141 tons without even a crack, and stood under that pressure for nearly one minute, when it broke.

" 3. Another similar block bore 104 tons.

" 4. One composed of nine sand to one cement bore 4½ tons.

" 5. One of equal quantities of sand and cement previously submitted to a pressure of 47 tons now cracked at that pressure, but ultimately bore a pressure of 108 tons before it broke down, the form of the crack not altering.

**Public Attention begins to be directed to Portland Cement.**—The rivalry between the two principal firms engaged in the manufacture of Portland cement, in what we may term the London district, had the effect of directing public attention to the new material, and the cement industry from this time steadily increased in importance. Fresh factories were started, and the quality gradually became more and more reliable.

**Early Experiments on the Strength of Cements.**—In a paper read by

Mr. G. F. White before the Institution of Civil Engineers in May, 1852, there is an account of the experiments, to which reference has already been made, at Messrs. Grissell's works in 1847, and of some additional tests carried out at Mr. Jackson's works on March 8, 1851. We quote certain of these results, as they are of importance as illustrating the relative merits of the artificial and natural cements made about that time. Each block was 9 inches square and 18 inches long, and it was tested by hydraulic pressure applied on the smaller ends, a surface of 81 square inches :—

| Nature of Block. | Age in Days. | Crushing force in Tons. | | Lbs. per sq. inch. |
|---|---|---|---|---|
| | | On 81 sq. ins. | On 144 sq. ins. | |
| 1. Pure Portland cement, | 30 | 75 | 133 | 2,074 |
| 2. { 1 Portland, 2 Sand, { Immersed in water for 7 days after making. | 52 | 45 | 80 | 1,244 |
| 3. { 1 Portland, 3 Sand, { Immersed in water as soon as made for 7 days. | 52 | 25 | 44 | 691 |
| 4. Pure Roman cement, | 30 | 27 | 48 | 746 |
| 5. { 1 Roman cement, 2 Sand, | 52 | 3 | 5·33 | 83 |
| 6.* { 1 Portland, 2 Sand, Concrete, | 48 | 24 | 42·6 | 664 |
| 7.* Concrete, | 270 | 63·75 | 113·33 | 1,763 |
| 8.* { 1 Portland, 3 Sand, | 70 | 16·875 | 30 | 442 |
| 9.* { 1 Portland, 10 Shingle, | 30 | 10 | 17·77 | 276 |

Experiments made at Mr. Jackson's works on blocks 6 inches by 6 inches, and 12 inches long :—

| Nature of Block. | Age in Days. | Crushing force in tons. | | Lbs. per sq in. |
|---|---|---|---|---|
| | | On area of 36 inches. | On the sq. ft. | |
| Pure Portland cement, | 40 | 40 | 160 | 2,453 |
| „ Atkinson's cement, | 40 | 20 | 80 | 1,244 |
| „ Sheppey cement, | 40 | 19·5 | 78 | 1,213 |
| „ Roman cement, | 40 | 13·25 | 53 | 829 |

* Experimental blocks 6, 7, 8, 9, described as concrete, of which cement and sand occupied one-fifth part in bulk.

It is argued from the first set of experiments that neat Portland cement is three times the strength of neat Roman cement, and that with two parts of sand Portland is half as strong again as neat Roman cement, while even with three parts of sand it is equal in strength to neat Roman cement.

**Experiments at the Exhibition of 1851.**—Some experiments tried at the great Exhibition in Hyde Park, before the Jury of Class XXVII. in September, 1851, are interesting, as the cement was used in the briquette form (see Fig. 1).

The breaking weight per square inch of neat Portland cement was 414 lbs., which is a very good result for that period. No indication is, however, given of the age of this sample.



Fig. 1.—Early Test Briquette.

**Prices of Roman and Portland Cement.**—The price of Roman cement had fallen about 1848 to 1s. 3d. per bushel, the original price having been 4s. 6d.; the cost of Portland cement at this time was, as we have seen, about 2s. 6d. per bushel.

**Mr. Johnson's Statement respecting the Manufacture.**—We think that we may here insert a very important statement respecting the early history of Portland cement, drawn up for one of the authors by the veteran cement manufacturer, Mr. I. C. Johnson,* in 1880, extracts from which were published in *The Building News* of that year. Mr. Johnson states that young Aspdin "began work at Rotherhithe in connection with Messrs. Maude & Son on a small scale, and did sometimes make a strong cement, but, owing to a want of scientific method, the quality as respects strength and durability was not to be depended upon." He proceeds :—

" I was at this time (about 1845) manager of the works of Messrs. White, at Swanscombe, making only the Roman cement, Keene's plaster, and Frost's cement, the latter composed of 2 chalk to 1 of Medway clay, calcined lightly, and weighing 70 to 80 lbs. per bushel.

" My employers, attracted by the flourish of trumpets that was then being made about the new cement, desired to be makers of it, and some

* On the 28th January, 1911, Mr. I. C. Johnson celebrated his 100th birthday, and to commemorate the event he had a handsome presentation made to him, by a deputation of the Portland Cement Trade, of a silver tea and coffee service and illuminated testimonials, but he did not long survive his centenary, as unfortunately he took a severe chill, from which he did not recover, but passed peacefully away on the 29th November, 1911.—*From the Autobiography of I. C. Johnson*, commenced by Mr. Johnson, but completed by his daughter. Publishers—Farncombe & Son, 30 Imperial Buildings, Ludgate Circus, E.C.
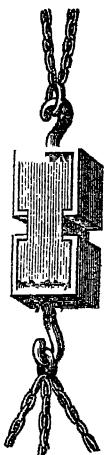
steps were taken to join Aspdin in the enterprise, but no agreement could be come to, especially as I advised my employers to leave the matter to me, fully believing that I could work it out.

"As I before said, there were no sources of information to assist me, for although Aspdin had works, there was no possibility of finding out what he was doing, because the place was closely built in, with walls some 20 feet high, and with no way into the works, excepting through the office.

"I am free to confess that if I could have got a clue in that direction I should have taken advantage of such an opportunity, but as I have since learned, and that from one of his later partners, the process was so mystified that anyone might get on the wrong scent—for even the workmen knew nothing, considering that the virtue consisted in something Aspdin did with his own hands."

**Aspdin's Secret Processes.**—Thus he had a kind of tray with several compartments, and in these he had powdered sulphate of copper, powdered limestone, and some other matters. When a layer of washed and dried slurry and the coke had been put into the kiln, he would go in and scatter some handfuls of these powders from time to time as the loading proceeded, so the whole thing was surrounded by mystery.

**Analysis of Aspdin's Cement.**—"What then did I do? I obtained some of the cement that was in common use, and, although I had paid some attention to chemistry, I would not trust myself to analyse it, but I took it to the most celebrated analyst of that day in London, and spent some two days with him. What do you think was the principal element, according to him? Sixty per cent. of phosphate of lime! All right, thought I, I have it now. I laid all the neighbouring butchers under contribution for bones, calcined them in the open air, creating a terrible nuisance by the smell, and made no end of mixtures with clay and other matters contained in the analysis, in different proportions and burnt to different degrees, and all without any good result."

**Attempt to produce a Cement from the Components of Roman Cement.**—"The question was, what was the next thing to be done? I had an idea that the elements were those contained in Roman cement, and I had read somewhere that the older chemists had taught that the value of Roman cements was due to the iron and manganese contained in them. I knew that these matters gave rise to the peculiar colour of Roman cement, but they were absent in Portland."

**Mr. Johnson's Experiments.**—I had a laboratory and appliances on the premises, so I worked night and day to find out the component parts of the stones from Harwich and Sheppey. Having found these, and having tried many experiments, spreading over some months, in putting different matters together, I began to think that lime and alumina were the chief ingredients necessary. I, therefore, tried quicklime powdered and mixed with clay

and calcined, by which means I got something nearer. It was a cement very much like Frost's. After this I used chalk and clay as used in Frost's cement, but with more chalk in proportion. The resulting compound being highly burned, swelled, and cracked.

" By mere accident, however, some of the burned stuff was clinkered, and, as I thought, useless, for I had heard Colonel Pasley say that he considered an artificial cement should feel quite warm after gauging, on putting your hand on it, and that in his experiments at Chatham he threw away all clinkers formed in the burning."

**Trial of Clinker formerly rejected.**—" However, I pulverised some of the clinker and gauged it. It did not seem as though it would harden at all, and no warmth was produced. I then made mixtures of the powdered clinker, and powdered lightly-burned stuff,* this did set, and soon became hard. On examining some days later the clinker only, I found it much harder than the mixture ; moreover, the colour was of a nice grey."

**Works conducted on a Larger Scale.**—" Supposing that I had nearly got hold of the right clue, I proceeded to operate on a larger scale, making my mixture of 5 of white chalk to 1 of Medway clay. This was well burned in considerable quantities, and was ground finely ; but it was, of course, a failure from excess of lime, although I did not then know the reason of it. The whole of this material was tossed away as useless into a kind of tunnel near at hand, and laid there for some months, after which I had the curiosity to take a sample of it and gauged it as before, when, to my astonishment, it gauged smoothly and pleasantly, and did not crack and blow as before, but became solid, and increased in hardness with time."

**Traces a Previous Failure to Excess of Lime.**—" Cogitating as to the cause of this difference, it occurred to me that there had been an excess of lime, and that this exposure in a rather damp place had caused the lime to slake.

" This was another step in advance, giving me, as it did, the idea of there being too much chalk, so I went on making different mixtures until I came to 5 of chalk and 2 of Medway clay, and this gave a result so satisfactory that hundreds of tons of cement so mixed were soon afterwards made. Some of this cement was sent to the French Government Works at Cherbourg, and was, as I believe, set up as a standard of quality to which all subsequent purveyors had to conform."

**Anticipates Process of Grinding with a Minimum of Water.**—Mr. Johnson subsequently explains how he partly anticipated Goreham's patent of grinding with a minimum of water, and he details his experiences as a cement maker on his own account, first at Frindsbury, near Rochester (where he established the first manufactory on the Medway), then at Cliffe, later at

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* Aspdin, we learn from one of his letters, made his cement form a mixture of tender and hard-burned clinker.

Gateshead-on-Tyne, where he followed Aspdin, who had failed in business, and lastly at Greenhithe.

**Last Traces of the Aspdins.**—We think that Mr. Johnson's account is very interesting as the personal narrative of one of the founders of the cement industry, and one to whom, as we shall see later, it owes some important improvements. In bringing this somewhat lengthy chapter to a close, we may mention that the elder Aspdin was still working at Wakefield in 1853, and we are informed by his grandson, Mr. W. A. Aspdin, that he resided there until his death in 1855. He was interred at St. John's Church, Wakefield, and his tombstone there bears the following inscription :—

> " Sacred to the memory of the late
> JOSEPH ASPDIN,
> of this town,
> Inventor of the Patent Portland Cement,
> Who departed this life on the 20th day of March, 1855,
> Aged 76 years."

A tribute to his memory was paid by B. H. Thwaite in an article in the *Yorkshire Weekly Post* of October 17, 1903, under the heading of " A Forgotten Genius." It concluded with a suggestion that a statue or memorial of some kind should be erected to his memory in Leeds, his native city. Some correspondence by G. R. Redgrave, J. T. Pullon, and R. Hauptmann followed in the *Yorkshire Daily Post*. The two first mentioned wrote in appreciation and promised support, the last named differed, disputing the originality of Aspdin's invention. Nothing came of the proposal.

Aspdin's grandson tells us that the works he originally built were pulled down for the railway, and other mills were erected, which were carried on after his death by his son, James. Joseph Aspdin had two sons and one daughter. His son, William, after his failure at Gateshead, went to Hamburg in 1856. The remainder of his life was long involved in obscurity, which was recently cleared up by F. Quietmeyer,[*] who made enquiries at Lüneburg. He was first associated with a Hamburg coal factor in the establishment of a cement works, previous negotiations with a Lüneburg lime-burner having fallen through. Leaving Hamburg he joined in the erection of another works in Lüneburg. The promised output here not reaching expectations led to his retirement, and leaving for Hamburg he raised capital for yet another venture at Lägerdorf, near Itzehoe. This formed the nucleus of a large plant now known as the Lägerdorfer Portland Zement-fabrik, an important branch of the Alsen Company. Difficulties here again caused his retirement, and he died in 1864, the result of a fall in the street at Itzehoe, in the 48th year of his age.

[*] *Zur Geschichte der Erfindung des Portlandzementes*, p. 182. Berlin, 1911.

A writer in· *The Builder* in March, 1880, states that, before the success
of Aspdin's new material was thoroughly assured, " he launched out by
renting several acres of land near Gravesend and commenced building
' Portland Hall ' in such an elaborate and artistic manner as to require
some £40,000 to bring it to completion. When the structure was rather
more than one-third up, he had to stop (for want of funds), and he sold off
at so great a sacrifice that he left the country and died abroad." His widow
wrote at a later date saying she kept a small school and was in great need,
but she omitted her address, so nothing could be done for her.

# CHAPTER VI.

## THE COMPOSITION OF PORTLAND CEMENT.

CONTENTS.—Influence of Materials on the Seat of the Trade—Essential Components of Cements—Proportions of the Ingredients—Quick-setting Cements—Over-limed Cements—Sulphur in Portland Cement—Magnesia in Portland Cement—Magnesia and its Effects on Roman and Rosendale Cements—Alkalies.

**Influence of Materials on the Seat of the Trade.**—The inducements originally offered to cement makers to settle in the Thames district are easy to understand, the ample supply of chalk and the excellent Medway mud were admirably adapted for their purpose, and, in course of time, a large colony of manufacturers established themselves on the banks of the Thames and Medway, and the London Portland cement obtained a wide reputation. Indeed, the belief gained ground that no really good cement could be made elsewhere, and the raw materials of this district were transferred at great expense to other less favoured localities in which the manufacture was carried on.

**Failures caused by Want of Chemical Knowledge.**—Owing to imperfect acquaintance with the chemistry of cements, the process was at first, as we have seen, exposed to continual dangers, and the failures of the cement made from the lias, and from the lower chalk, were at one time so serious as to appear likely to bring all other cements into discredit. The constant fluctuations in the thin beds of stone and shale in the lias formation, and the varying quantities of clay combined with the lower or grey chalk, led the cement maker who relied upon rule-of-thumb into all kinds of difficulties and dangers. Too often he depended on some cunning workman, who made a mystery of his proportions, and concealed his ignorance and accounted for his failures by statements which the master took upon trust or did not venture to dispute.

**An Early Authority on Cement Making.**—We remember, in the early sixties, such an authority in one of the older works on the Medway, who had washed whole backs full of over-limed slurry (the liquid mixture of chalk and clay), and who attributed the " blowing " of the resultant cement to an unpropitious state of the atmosphere. The real fact of the matter being that some new beds of chalk were being quarried which contained only 5 per cent. of clay, instead of the 10 per cent. present in the chalk to which he had

4

been accustomed, and he had dealt with the new chalk just as he did with the old.

**Materials available for Cement-making.**—It is now perfectly well known that suitable mixtures of carbonate of lime and clay can be prepared from raw materials, to be found in all parts of the world, and in many geological formations. It is not essential that the mixture should be made of each of these materials in the pure state. They occur naturally compounded in various proportions in vast beds in many different localities, and in making use of such materials, all that is necessary is to employ them in such proportions as will give the required quantity of carbonate of lime in the mixture.

As examples of pure or nearly pure materials, we may instance the white chalk of the Thames district, the indurated chalk of the North of Ireland, and many deposits of the carboniferous limestone formation, all of which contain about 98 per cent. of carbonate of lime. Among the clays and shales in use for cement-making (under the latter term we imply a solid form of clay compacted by pressure and capable of being split into laminæ), we have the alluvial mud of the Medway—a salt water deposit—the freshwater alluvium found on the banks of many rivers, boulder clay, the shales and clays of the coal measures, and the shales of the Silurian formation, in which last lime is generally either absent or present in small quantity. As instances of naturally compounded materials, we may mention the lower or grey chalk of the Medway, the limestones and shales of the lias and of the lower carboniferous strata, gault clay, the chalk marls of Cambridgeshire, Belgium and Germany, and the Silurian limestones so extensively used in the Lehigh Valley district of Pennsylvania.

**The Present Position of the Cement Manufacturer.**—From the point of view simply of materials, we have now entered upon a phase of the Portland cement manufacture in which the trade has passed far beyond the boundaries of the Thames and Medway districts, and has spread over the whole world. In this country to-day the tendency is to seek for a cheap and abundant source of raw materials with facilities for transport of the product, and to establish works in the immediate vicinity of large centres of population, where the cement is likely to be locally required. The factories established at various seaports in the North, depending on imported chalk, work at a great disadvantage as regards cost of raw materials, and in some cases have been closed.

**The Constituents of Portland Cement.**—It will be well, before we treat of the various processes of manufacture, if we examine somewhat in detail the actual constituents of Portland cement, calling attention, first, to those substances the presence of which is essential, and subsequently to certain other ingredients present in the raw materials which either exert little influence upon the mixture, or which in certain cases, or when they exist in large quantities, may be productive of positive injury. The constitution

of Portland cement, or the manner in which the raw materials are combined, or are supposed to be combined, will be considered in a subsequent chapter.

**Essential Components of Cement.**—Careful experiments have proved that the only essential components of Portland cement are lime, alumina, and silica, which substances we have dealt with in our introductory chapter; but there are, secondly, as we have seen, numerous other ingredients present, occurring either as impurities in the clay, or in certain cases derived from the fuel used for calcination, some of them tending to facilitate the cement action, others either inert in themselves or merely taking the place of the essential constituents, and lastly certain substances which we must regard as injurious, except when they are found in very small quantities.

**Characteristics of Clays adapted for Cement-making.**—The best clays for the use of the cement-maker are those that are highly siliceous, even if much of the silica occurs in the free state as sand. Should it be present as a coarse-grained sand, the mixture requires to be very perfect and finely ground. If this is done, experience shows that in the finished cement the silica, even from a sandy clay, is found in the soluble condition. This is not the case in burning such clayey substances into a hydraulic lime, as the temperature reached is not sufficiently high entirely to effect this change. The proportion of silica present should at least equal $2\frac{1}{2}$ times the amount of the alumina and iron oxide taken together. Thus clay containing 18 per cent. of alumina and 7 per cent. of iron oxide should contain 64 per cent. of silica. Clays of this composition require a high temperature to effect their fusion when they are employed in conjunction with carbonate of lime. The resulting cement sets in a reasonable time, rapidly attains sufficient strength to give good breaking tests, and steadily increases in strength with age. On the other hand, clays with a high percentage of alumina yield a much more fusible mixture, which can be calcined with less fuel, but which often causes trouble in the kiln by overburning. The resulting cement sets quickly, often indeed with such rapidity as to render its use difficult without re-gauging, while the strength at short dates runs high. There is little increase of strength with age, indeed often a tendency to retrogression. Clays high in alumina and low in silica may be rendered quite satisfactory by the addition of silica in some form, such as sand or sandstone, of course before grinding. This fact has been disputed, but it has been and is being done. We ourselves have done it with complete success.

**Proportions of the Ingredients.**—The actual percentage of clay which may be added to the carbonate of lime to produce Portland cement varies between somewhat wide and not very clearly defined limits. The exact quantity depends upon the relation of silica to alumina, and the care taken in the manufacture. All mixtures which contain from 74 to 77 per cent. of carbonate of lime will, when carefully and intimately mixed and finely ground, produce, if sufficiently calcined, Portland cement of good quality.

A high percentage may be used with clay rich in silica, but it will fall within these limits. In calculating the proportions, magnesia, if present in more than small quantity, should be considered as replacing lime, the quantity of which should be correspondingly reduced. This will again be referred to in a later chapter.

When the percentage of bases (lime and magnesia) in the unburned mixture falls below about 74 per cent. a cement is obtained which is technically termed overclayed. Compounds of this nature, if burned at the temperature necessary for the production of sound hard clinker (the term applied to the semi-fused material issuing from the kiln), fall to dust on cooling. The resulting cement is light in weight, is apt to set quickly, has a brownish colour, and never becomes thoroughly indurated. These light descriptions of Portland have a tendency to crumble on exposure to the weather.

**Quick-setting Cements well adapted for Plasterers' Work.**—They are essentially plasterers' cements, as they work readily under the float or trowel, and, owing to the fact that they set more speedily than a dense cement, the workman can leave them within reasonable time, which he appears very often to be unable to do when using a dense slow-setting sample of Portland. These over-clayed cements are now but rarely made, except perhaps accidentally, although at one time, especially the period of stucco architecture in London, they were much sought after and preferred for some descriptions of work. There is, however, now but little demand for cements of this type, which in some cases approached the Roman cements in composition, since the finely ground Portland now made sets sufficiently quickly for all practical purposes. It was the fraudulent substitution of cement of defective quality of the above character, often prepared from slack burned clinker, which for a time had a prominent part in bringing true Portland cement into disrepute. There was formerly, when the true characteristics of Portland were less widely known, a great temptation to aim at the production of these light cements, as they are ground with comparative ease, and they enabled the cement-maker to dispose of his insufficiently burned material without further calcination.

**Over-limed Cements.**—On the other hand, the presence of an excess of lime—that is, when the percentage of carbonate of lime in the raw material ranges from 77 to 78 per cent.—leads to a cement which will stand the highest temperature of the kiln and, in fact, necessitates very heavy burning. Such cements are extremely dense when burned at a high temperature, they set very slowly and are difficult to grind. Looking to the high tests now demanded, manufacturers are inclined to raise to the utmost limit of safety the percentage of lime, and thus to approach more and more to the danger point of unsoundness. This danger is avoided by extremely fine grinding, both of the raw material and of the finished cement, and by hard burning. Unsoundness, within certain limits, may be corrected by

storage in silos previous to use, but, at the present time, the manufacture is generally so carefully conducted as to allow of the use of Portland cement direct from the mills, although some specifications still require a period of storage.

**Iron in Portland Cement.**—The colour of Portland cement is due to the presence of compounds of iron. It occurs principally in the state of the higher oxide, $Fe_2O_3$, but a small quantity of the lower oxide, $FeO$, is generally present. Some chemists, however, speak with certainty of combinations with lime in which the iron functions as an acid to form ferrites of lime. During calcination its action is that of a flux.

**Calcium Sulphate.**—It is in this form that the greater part of the sulphur exists in Portland cement. Its presence has been considered detrimental, and attempts have been made in specifications to fix the amount permissible as low as 1 per cent., a condition that few if any cements could fulfil. Its action in regulating the setting time is now so fully recognised that most specifications allow an addition to the clinker when grinding of such a quantity as will make with that naturally occurring a total not exceeding 2 to 3 per cent. of anhydrous sulphuric acid—$SO_3$. Although the action of calcium sulphate, in small quantities, is thus shown to be beneficial, there can be no doubt but that the presence of this substance in proportions exceeding, say, 4 or 5 per cent. is injurious, for we must remember that calcium sulphate is soluble in water, and in damp situations much of it would inevitably be washed out of the mortar and, moreover, this substance never attains to any considerable degree of hardness.

**Selenitic Action.**—The action of calcium sulphate on cement was discovered in 1854 by the late Major-General Scott, C.B., F.R.S., the inventor of selenitic cement, and in the so-called Scott's cement patented by him in 1856, this property was for the first time turned to commercial account. To General Scott, moreover, we owe the proposal to add calcium sulphate to Portland cement for the purpose of retarding the setting period. We shall treat of the selenitic cement in a later chapter.

Sulphuric acid, when present in Portland cement, acts, it is believed, in the manner described in the case of selenitic cement upon the uncombined lime present, and deprives it of its avidity for water, causing it to set after the nature of a cement. Very small quantities of sulphuric acid will delay the rapidity of the initial set of Portland cement, and we have found, in the case of a fiery cement, that the addition to it of 1 per cent. of its weight of plaster of Paris would delay the time needed to set from five to seven hours.

**Messrs. Dyckerhoff's Experiments.**—The annexed table, extracted from the *Proceedings of the Institution of Civil Engineers*, gives the results of some important experiments by Messrs. Dyckerhoff bearing upon this question. They demonstrated that, together with the delayed setting time, a great

TABLE SHOWING GAIN IN STRENGTH WHICH RESULTS FROM AN INCREASE IN SETTING TIME.

| No. | SAME KIND OF CEMENT. | Time of Setting Neat. | Neat Cement 25 parts Water to 100 parts Cement. | | | | | One Cement to three of Standard Sand. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | One Week. | Four Weeks. | Twelve Weeks. | Twenty-five Weeks. | Fifty-two Weeks. | One Week. | Four Weeks. | Twelve Weeks. | Twenty-six Weeks. | Fifty-two Weeks. |
| 1. | Original Cement, | Minutes, 20 | 322·9 | 405·5 | 517·9 | 621·7 | 701·4 | 115·2 | 167·9 | 237·6 | 301·6 | 359·9 |
| 2. | The same Cement with ½ per cent. of Gypsum, | 210 | 315·8 | 456·7 | 573·4 | 624·6 | 651·6 | 142·3 | 212·0 | 338·6 | 352·8 | 389·8 |
| 3. | The same Cement with 1 per cent. of Gypsum, | 600 | 375·6 | 507·9 | 567·7 | 697·2 | 781·1 | 159·3 | 237·6 | 311·6 | 368·5 | 384·2 |
| 4. | The same Cement with 2 per cent. of Gypsum, | 840 | 425·4 | 543·5 | 688·6 | 718·5 | 806·7 | 180·7 | 263·2 | 304·4 | 374·2 | 409·7 |
| 5. | The same Cement without Gypsum but kept in store for some months, | 630 | 317·3 | 449·6 | 550·6 | 593·3 | 618·9 | 167·9 | 219·1 | 318·7 | 359·9 | 431·1 |

*Note.*—No. 1 weighed about 110·7 lbs. per bushel. No. 5 about 105·9 lbs. per bushel of 40 litres. The breaking weights are given in lbs. per square inch.

gain in strength results from the use of trifling additions of gypsum. In fact, this treatment is equivalent to, and may replace the aeration which dense highly calcined cements require previous to use; this statement being clearly proved by the bottom row of figures. General Scott pointed out that the same results could be obtained by exposing the cement to the action of a jet of steam which rapidly hydrates the free lime. Indeed, in one of his numerous patents he specifies this process.

**Calcium Sulphide.**—Although calcium sulphate, in small quantity, has its value in the cement, sulphur compounds, unless occurring in small proportions, are objectionable in the raw materials. Their tendency is to undergo decomposition in the kiln, resulting in the formation of calcium sulphide, a most dangerous ingredient of Portland cement, although it is always present, but generally in quantity too small to be harmful, often only in traces. The troubles that arise from its presence in excess are due to its property of reacting with the iron compounds, forming iron sulphide. This substance attracts oxygen, with the result that the cement assumes a brown colour. This action continues with much greater rapidity in the gauged cement than it does before it is mixed. Test briquettes have a greenish tint when broken, and the fractured surfaces on exposure to the air change to a rusty brown. The set of cements of this type is very slow, even when water is sparingly used in gauging them; with an excess of water they will scarcely set at all, and they never attain a high tensile strength, especially under the sand test. The Specification of the French Ministry of Public Works allows only a trace of sulphur as sulphide.

**Magnesia in Portland Cement.**—Magnesia in small quantity is harmless, and may be neglected. The British Standard Specification permits an amount not exceeding 3 per cent., but few English cements contain as much as this. Of its action in larger quantities the following instances may be given. Cement made at Campbon de la Loire, France, from a local limestone, was used in the construction of three railway bridges over the River Oust, and in the abutments of a bridge at Nantes. Twelve months after completion, in 1881, expansion began to develop, finally resulting in the destruction of the structures. Boulogne cement used for similar work under the same conditions remained perfect. Samples of the Campbon cement were found to contain from 16 to 28 per cent. of magnesia. Vicat seems to have been in error here. In his Recherches Statistiques, he reports the limestones of Campbon as feebly hydraulic and containing about 6 per cent. of magnesia. Test samples made of mixtures of Boulogne cement and magnesia, and immersed in water, expanded in proportion to their content of magnesia. In the Law Courts, and in a Church, at Cassel, a similar failure occurred following the use of cement which was found to contain 22 per cent. of magnesia.

This subject excited great interest, and much research by many

investigators resulted in conflicting opinions. H. Le Chatelier considered that magnesia could replace lime in Portland cement, Dr. Erdmenger that it could not. The Association of German Portland Cement Manufacturers appointed a Committee, of which Dr. Dyckerhoff was President, to investigate the subject. The majority reported that their investigations proved that a content of not more than 8 per cent. was harmless. The President differed, stating in a minority report that a quantity exceeding 4 per cent., whether as an addition to a normal cement or substituted for lime in its composition, caused expansion, a falling off in strength and unsoundness. The results of his experiments are shown graphically in three diagrams in the report.*

In the United States, this subject has been investigated by Messrs. Newberry, Clifford Richardson, and P. H. Bates among others, the last-named by petrographic methods. The question is still unsettled. A distinction, not always made, must be drawn between magnesia as an addition to a normal cement, or as a constituent of the raw materials. Magnesium carbonate, when calcined at a temperature much lower than that required for lime, loses its carbonic acid and becomes caustic magnesia, which during hydration increases in volume as lime does, but it does so more slowly. In the caustic state, if added to a normal cement, it would cause expansion after the mixture had hardened, due to its slow hydration, but it might not produce disintegration if present in moderate quantity. At a temperature approaching that at which Portland cement is burned, unlike lime, it sinters, and in this state hydrates after a very considerable lapse of time. If added to normal cement, expansion and ultimate destruction must occur. The conditions are different when magnesia in excess forms one of the constituents of the raw materials. During calcination it combines with silica and alumina. These compounds have the same molecular constitution as those with lime, but they become hydrated much more slowly than the lime compounds. It has been found, by laboratory experiments, that silicates and aluminates of magnesia acquire on hydration a superior degree of hardness to the similar compounds of lime, and that they remain wholly unaltered under water. It is possible that cement mortars, which consist of a mixture of the silicates and aluminates of lime and of magnesia, may, after the hardening of the lime silicates, undergo molecular changes due to the deferred hydration of the magnesia compounds, and this may disturb the original cohesion of the mass, and result in its disruption.

**Roman and Rosendale Cements.**—In the lightly-burned cements of the Roman cement type, and in the Rosendale cement of the United States of America, described at p. 30, the magnesia is found to be quite harmless, due to the low temperature at which they are burned. It will be seen from the annexed analyses of American cement stones of the Rosendale type

* *Protokoll der Verhandlungen des Vereins Deutscher Portland-Cement-Fabrikanten,* 1895.

that many of these materials contain a large percentage of magnesia in addition to lime and alkalies, and that the proportion of silica and alumina is low as compared with our English quick-setting cements, as, for instance, those made from the septaria of Harwich and the Isle of Sheppey, some analyses of which are added for the purpose of comparison.

ANALYSES OF NATURAL CEMENT STONES.

|  | Layer No. 9, Rosendale. | Layer No. 13, Rosendale. | Layer No. 17, Rosendale. | Sheppey Island Septaria. | Harwich Septaria. |
|---|---|---|---|---|---|
| Carbonate of lime, . . . | 43·30 | 28·48 | 40·00 | 63·00 | 60·5 |
| Carbonate of magnesia, . . | 26·04 | 32·86 | 39·04 | 4·2 | 5·7 |
| Silica, clay, and insoluble silicates, | 18·52 | 26·00 | 11·10 | } 32·00 | 33·0 |
| Alumina, . . . . . | 2·18 | 4·64 | 2·52 |  |  |
| Peroxide of iron, . . . | 1·86 | 1·86 | 1·42 |  |  |
| Sulphuric acid, . . . . | 1·96 | 1·18 | 0·22 | .. | .. |
| Potash and soda (chloride), . . | 4·24 | 4·72 | 4·06 | 0·8 | 0·8 |
| Water and loss, . . . . | 0·20 | 0·26 | 0·26 | .. | .. |
| Total, . . . . | 98·30 | 100·00 | 98·62 | 100·00 | 100·00 |

**Alkalies in Portland Cement.**—We have still to glance at the action of the alkalies which we regard as very important constituents of the cement. The only alkalies found in Portland and nearly always present in good samples, to the extent of from 0·5 to rather over 1·0 per cent., are potash and soda. These substances are derived mainly from the clays or clay shales, and while their action is most valuable during the calcination they are also beneficial, we believe, at the time of gauging the cement, for the alkaline silicates, as it is well known, are the only compounds with silica soluble in water. Their office as carriers of silicic acid to the lime and other sparingly soluble ingredients of the cement has, we think, not hitherto been sufficiently studied, and when considering the set of cements and the recent theories respecting this much-debated question, the alkalies should not be overlooked.

**The Investigations of Fuchs.**—It will be sufficient here to allude briefly to the investigations of Fuchs, who demonstrated very clearly the influence of these substances. Thus he found that decomposed felspar when treated in the humid way with caustic lime parted with 10 per cent.—that is to say, nearly the whole—of its potash; he found further that substances containing but little alkaline matter, such as pumice-stone and pitch-stone, were deprived of the same by lime, and that both lithia and potash could be separated in this manner from lepidolite (a silicate of alumina, lithia, and potash). By a similar process the alkali is separated from most varieties of clay and transferred to the lime. The solubility of alumina and gelatinous

silica in potash renders it more than probable that the alkalies accelerate
the hydraulic action of the lime by promoting and facilitating the gradual
transference to it of the silica.

**Kuhlmann's Experiments.**—Kuhlmann carried out numerous experi-
ments with the alkaline silicates constituting " water-glass," which established
the fact that these materials part with their silica to the lime without the
aid of heat, and the same reaction occurs with carbonate and sulphate of
lime as with caustic lime—the alkali transfers its silica to the lime and unites
with the carbonic or sulphuric acids. Chalk powder exposed to a solution
of silicate of potash becomes after a short time solidified into a stone-like
mass, and a lump of chalk immersed in the liquid receives a surface coating
of silicate of lime, which on subsequent exposure to the air becomes so hard
that it is capable of taking a polish. The induration of cement concrete
by means of the so-called " silica-bath " depends upon this property, and
the preservation of wall surfaces of stucco by a coating of water-glass is
another illustration of this principle.

# CHAPTER VII.

## THE CHEMICAL ANALYSIS OF CEMENT RAW MATERIALS, PORTLAND CEMENT, AND LIME.

CONTENTS.—Sampling—Preparation of the Samples for Analysis—Results required from the Analysis—Analysis of Limestone—Portland Cement Mixtures—Clay and Shale—Portland Cement—Lime—Gypsum—Determination of Lime by Titration with Permanganate—Adulteration of Portland Cement—Tables of Atomic Weights and Factors.

**Sampling.**—When sampling, in the field or quarry, it should be remembered that the composition of the rock may vary at different levels. This is especially the case in the stratified beds of the lias and lower carboniferous rocks in which the percentage of carbonate of lime may vary in each layer. It is sometimes not great, but sufficient to upset a cement mixture. The variation in the parting beds of shale when they occur is generally considerable. Samples may often be obtained by drilling. If the beds are stratified and in sight, many chips should be broken from each through their whole depth, taking care to avoid the shale beds if they are present. These should be sampled and analysed separately. In actual work, it may be necessary to clean the stone when quarried from adhering shale or clay; this operation will be referred to in a succeeding chapter. In soft materials, such as some varieties of chalk, and in marl or clay, cores may be obtained by the use of an auger.

During the process of manufacture, except in the case of the adjustment basins of the wet process, the contents of which are kept in motion, and from which samples may be dipped, routine samples should whenever possible be continuous ones. Either a stream of slurry, or of dry raw material, may be sampled continuously by a small elevator or worm constantly withdrawing to a receptacle a fraction from the main stream.

**Preparation of the Samples for Analysis.**—In the case of hard rock, the samples should be enclosed within a métal ring resting upon a hard steel plate, and be broken with a steel hammer to such a size that the largest pieces would about pass a sieve having a mesh of ¼ inch, but a sieve should not be used. The object of the ring is to avoid the risk of loss by flying fragments. The crushed material is thoroughly mixed, and then spread out in a thin layer which is divided into four quarters. Three of these are

rejected, the fourth is again broken down to a smaller size, and the operation of quartering repeated until the required quantity, which may be from 20 to 30 grammes, is obtained in the state of coarse powder, which is preserved in a stoppered bottle. If it is required to know the content of quarry moisture a portion of this should be taken for the determination. For the analysis, about 10 grammes are reduced to a very fine powder in a diamond steel mortar by blows upon the pestle with a hammer, avoiding any rubbing action, or it may be ground in the usual manner in an agate mortar. The fine powder is dried at a temperature of from 100° to 105° C., and is transferred to a stoppered weighing tube. In soft absorbent materials the water is usually determined. For this, portions of the sample are preserved in a stoppered bottle, at the time when taken. The bulk is dried, and prepared for analysis, as in the previous case.

**Results required from the Analyses.**—For technical purposes, the determination of minor constituents occurring only in small quantity and such as are without influence is not necessary, and they will not be considered here, as they do not interfere with the general accuracy of the results. For instance, the precipitate by ammonium hydrate, generally reported as oxides of iron and aluminium, will contain the oxide of phosphorus and that of manganese, if these oxides are present in the sample under analysis. Again, titanium is widely distributed in nature, and is a constituent of many clays, although usually in small quantity. If present, it will be found partially with the precipitate by ammonium hydrate, partially with the silica. For the exhaustive analysis of rocks and minerals the works mentioned at the foot of this page should be consulted.*

**Analysis of Limestone and Portland Cement Mixtures.**—From the stoppered tube, the following quantities are weighed off :—

1. From 0·5 to 1 gramme for the determination of silica, oxide of iron, alumina, lime, magnesia. This quantity to be transferred to a platinum crucible.

2. About 1 gramme for total sulphur, transferred either to a flask or a platinum crucible, according to which method of determination is decided upon.

3. About 1 gramme for sulphur existing as sulphate, transferred to a platinum or porcelain evaporating dish.

4. About 4 grammes for potash and soda, transferred to a glazed porcelain mortar of about 100 c.c. capacity.

5. About 1 gramme for carbon dioxide, transferred to the evolution flask of the apparatus employed for the determination.

* *The Analysis of Silicate and Carbonate Rocks.* W. F. Hillebrand. Washington Government Printing Office, 1916.
*Manual of the Chemical Analysis of Rocks.* Henry Washington. London, Chapman & Hall, 1904.

**Quantity No. 1**—*Determination of Silica.*—It was formerly considered that the presence of silica in the insoluble form as sand was detrimental in Portland cement mixtures, and sandy materials were rejected. With coarse sand this is still true, but, as we have previously explained, if in an extremely fine state of division it is brought into the soluble form by the action of the lime at the temperature of the kiln. It is, therefore, not necessary to determine separately the silica present in the insoluble state. If a temperature of from 1,100° to 1,200° can be obtained in the laboratory by the use of a powerful blast lamp, a muffle or an electric furnace, it may all be separated in the soluble condition by prolonged ignition of the portion taken for analysis. If this is not possible, or if the result is doubtful, a quantity of fusion mixture, or of pure dry sodium carbonate equal to one-half the weight of the quantity taken for the analysis, should be added to it in the platinum crucible, both substances being thoroughly incorporated by mixing with a glass rod having a rounded end. The crucible is now strongly heated by a blast lamp, or in a furnace, until the contents are sintered. A liquid fusion will not be obtained, and it is not necessary to use a larger quantity of the flux to obtain one. Decomposition is complete when sintering has occurred. When cold, the contents of the crucible are turned out into a platinum dish, and triturated with a little water, using a glass rod to break up the lumps. The crucible is rinsed with a little dilute hydrochloric acid, and washed out into the dish, which should be kept covered with a clock glass.   Dilute hydrochloric acid is added in slight excess, and the dish is gently heated for a few minutes until the evolution of carbon dioxide ceases. The contents are evaporated to dryness on a water-bath, the drying being completed by strongly heating on a sand-bath for an hour. When cold, the contents of dish are moistened with a few drops of strong hydrochloric acid, the dish is covered and set aside for ten minutes. Water is added, the contents of dish heated, filtered, and the precipitate well washed with hot water. One evaporation is not sufficient to separate entirely the silica. The filtrate is evaporated to complete dryness, and treated exactly as in the first instance, the silica being collected and washed on a separate filter. Both precipitates are strongly ignited together in a platinum crucible, and weighed.

**Determination of the Oxides of Iron and Aluminium.**—The filtrate from the silica is boiled, after the addition of a few drops of bromine water, or nitric acid, and allowed to cool. It is then heated to boiling, after the addition in slight excess of ammonium hydrate free from carbonate. The voluminous precipitate of ferric and aluminium hydroxides settles slowly, but filters rapidly without the aid of a filter pump—a piece of apparatus, by the way, that the writers dislike—and nothing is gained by allowing it to settle, and washing by decantation. It is washed twice on the filter with hot water, the filtrate and washings, which should be received in a beaker of ample capacity, being set aside. The precipitate is washed out of the filter into the

beaker in which the precipitation was originally effected, and is dissolved by heating with a little dilute hydrochloric acid. Ammonium hydrate is added in slight excess, and the solution with precipitate is heated to boiling. The precipitation is filtered off and well washed with hot water, the filtrate and washings being received in the beaker containing the filtrate from the first precipitation. Care should be taken that this precipitate is sufficiently washed, as it retains traces of lime with great obstinacy. A small quantity of the washings should be collected in a test tube, to which a drop of ammonium oxalate is added, the contents of the tube are boiled, and the tube with contents is cooled by immersion in water, as traces of calcium oxalate do not separate from a hot solution. If lime is present, the contents of the test tube are washed into the beaker containing the filtrate, and the washing is continued until a sample of the washings give no trace of lime when tested as described. The second precipitation should never be omitted. The precipitate is ignited in a platinum crucible, and weighed. The filtrate is heated to boiling, sufficient boiling solution of ammonium oxalate is added to convert all the lime and magnesia present into oxalates, and the boiling is continued for two or three minutes. This treatment produces a granular precipitate which settles rapidly, and filters readily. The beaker with contents is set aside, until quite cold.

**Separation of the Oxides of Iron and Aluminium.**—The ignited precipitate of mixed oxides is fused in the platinum crucible at a low temperature with acid potassium sulphate. The melt is dissolved in hot water, with the addition of a little dilute sulphuric acid, and is transferred to a flask fitted with an evolution tube, in which is a Bunsen valve. The solution is reduced by zinc, and the iron determined by titration with standard permanganate. The alumina is taken by difference. Titanium is reduced by the action of nascent hydrogen, if it is present, and zinc is employed for reduction, the result for iron will be slightly high. Exact results may be obtained by reducing with hydrogen sulphide, boiling off the excess in a stream of carbon dioxide, and titrating with permanganate. If preferred, the iron may be determined gravimetrically by the following method:—The solution containing the mixed oxides after fusion is allowed to fall drop by drop with constant stirring into a strong hot solution of pure sodium hydrate, contained in a porcelain dish. The contents of the dish are boiled, diluted considerably with water, filtered, and the precipitate repeatedly washed with hot water. It is dissolved on the filter with a little dilute hydrochloric acid, ammonium hydrate is added to the solution in slight excess, the solution heated to boiling, filtered, the precipitate again repeatedly washed with hot water, dried, ignited, and weighed. It is very difficult to free this precipitate from traces of alkali.

The alumina may, if desired, be determined in the filtrate from the above. The filtrates and washings are rendered slightly acid with hydrochloric

acid, and the solution is concentrated considerably. Ammonium hydrate is then added, drop by drop, until the solution is very slightly alkaline. It is then boiled until a strip of moist turmeric paper held in the steam does not turn brown. The precipitate is filtered off, repeatedly washed with hot water, dried, and strongly ignited in a platinum crucible until the weight is constant.

**Determination of Lime.**—One precipitation does not effect a perfect separation of lime and magnesia, but a second one is often omitted. For accurate work, it should always be made. The supernatant liquid from the precipitate of calcium oxalate is decanted over a filter, and the precipitate is washed four times by decantation. The filter is washed out into the beaker in which the precipitation was made, the precipitate is dissolved by heating with dilute hydrochloric acid, the solution is rendered alkaline with ammonium hydrate, and boiled after the addition of a few drops of ammonium oxalate. The beaker with contents is allowed to become cold, the clear liquid is then decanted over the previous filter, the precipitate washed three or four times by decantation, finally transferred to the filter and well washed. The washing should be with cold water, as calcium oxalate is slightly soluble in hot. The precipitate is strongly ignited over a blast lamp or in a furnace to constant weight, and weighed as caustic lime.

If preferred, the lime may be weighed as carbonate, but the operation requires care. We ourselves have always employed this method. The precipitate is dried in the steam oven, separated as far as possible from the paper, which is completely incinerated in a coil of platinum wire ; the ash together with the precipitate is then heated for a moment to very low redness in a platinum crucible. Care should be taken to avoid overheating the crucible. The transition from oxalate to carbonate is indicated by the blackening of the precipitate, the colour immediately changing to pale grey or white. The contents of crucible, when cold, are moistened with a few drops of a saturated solution of ammonium carbonate, and carefully evaporated to dryness at a gentle heat. The crucible is then strongly heated on a hot plate for a few minutes and, when cold, weighed with its contents.

**Determination of Magnesia.**—The filtrate and washings from the calcium oxalate are concentrated to about 300 c.c. and allowed to become cold. The solution is made strongly ammoniacal, and solution of sodium phosphate is added with constant stirring as long as a precipitate continues to form. The sodium phosphate should be added in slight excess. The beaker is set aside for twelve hours, when the precipitate is filtered off and washed with a mixture of 3 parts water to 1 of ammonium hydrate of ·96 sp. gr., until a little of the washings rendered slightly acid with nitric acid gives no opalescence on the addition of a few drops of a solution of silver nitrate. This precipitate may not be of strictly normal composition, especially if precipitated from a solution containing ammonia salts in considerable quantity.

It is dissolved on the filter with a little hot dilute hydrochloric acid, and the filter is well washed. To the solution, which should not exceed 100 c.c., a few drops of sodium phosphate solution are added, and ammonium hydrate to strongly alkaline reaction. It is well stirred, and set aside for an hour. The precipitate is filtered off and washed exactly as in the first precipitation. It is dried, separated from the filter, and transferred to a platinum crucible. The filter is completely incinerated in a coil of platinum wire, the ash being allowed to fall upon the precipitate. The crucible is ignited, at first, gently, finally, at the full heat of a blast lamp. The magnesia is weighed as pyrophosphate. Some analysts prefer to get rid of ammonia salts in the filtrate from the calcium oxalate before precipitating the magnesia. A method for effecting this is given in the section on the determination of the alkalies.

Now that most specifications limit the quantity of magnesia in Portland cement, often allowing only a very small percentage, it is important that this constituent should be accurately determined. The British Standard Specification allows a quantity not exceeding 3 per cent.

**Quantity No. 2.—Determination of Total Sulphur.**—Two methods are available (*a*) by oxidation with nitric acid or other oxidising reagents, or (*b*) by fusing with an oxidising fusion mixture, the sulphur in each case being converted into sulphuric acid.

(*a*) *By Oxidation in the Wet Way.*—A little water and dilute hydrochloric acid are added to the weighed quantity in flask to expel carbon dioxide. As small a quantity as possible should be used. Strong fuming nitric acid is then added, and the flask is gently heated on a water-bath, a little powdered chlorate of potash is added in small portions, a small funnel being placed in the mouth of flask to avoid loss by spirting. When the oxidation is judged to be complete, the contents of flask are washed out into a porcelain dish, a little chloride of sodium is added, and the contents of the dish are evaporated to dryness. When cold, a little strong hydrochloric acid is added, and the solution is again evaporated to dryness. The nitric is replaced by hydrochloric acid by repeating this operation once or twice, and the residue is finally taken up with hydrochloric acid as in the separation of silica. Water is added, and the residue is filtered off. The filtrate is boiled, a little boiling solution of barium chloride is added, and the boiling is continued for a few minutes. The beaker is set aside for a few hours, the precipitate is then filtered off, washed, ignited, and weighed.

(*b*) The weighed quantity in the platinum crucible is mixed, by stirring with a glass rod, with a little fusion mixture, composed of four parts of sodium carbonate to one part of potassium nitrate, and is fused at a gentle heat. This fusion is best done with a Berzelius or a Swedish lamp. If coal gas is used, care must be taken that the contents of the crucible are not contaminated with sulphur from the flame; the lower part of the crucible should be inserted into a hole cut in a piece of asbestos millboard, which

it should accurately fit. When cold, the melt is boiled out with water, and evaporated to complete dryness, after the addition of hydrochloric acid. The residue is taken up with hydrochloric acid and water, and filtered off. The sulphuric acid is determined in the filtrate as in (*a*).

**Quantity No. 3—Sulphur occurring as Sulphuric Acid.**—The quantity in the beaker is treated with a little water and dilute hydrochloric acid, and is heated to expel carbon dioxide. The precipitate is filtered off, and the sulphuric acid is determined in the filtrate in the manner previously described. The sulphuric acid found here exists most probably in combination with lime as calcium sulphate, and to this it is usually calculated. Its percentage is deducted from the percentage found in the quantity taken for total sulphur. From the difference, the sulphur present as sulphide is calculated to iron sulphate, $FeS_2$. Care should be taken that the reagents used for these determinations are themselves free from sulphur.

**Quantity No. 4—Determination of the Alkali Metals.**—These have hitherto not been generally determined in cement, or in cement raw materials, but it is possible, that in view of the recovery of potash from the dust suspended in the gases from rotary kilns, more attention will be paid to them. In the summary of analysis results they are often returned as by difference, the summation being stated as 1·00. Thus they have to bear the weight of impurities in the reagents, and the plus or minus errors of every step of the analysis. Analyses adding up to exactly 100 are always open to suspicion. Constituents not determined should be described. W. F. Hillebrand says that if all are determined a summation should be reached within the limits of 99·75 and 100·5, Dr. Washington extends the allowable limits to from 99·5 to 100·75.

The method generally employed for determining potash and soda in silicates is that of Professor Laurence Smith,* which is most accessible for reference in the summaries by Sir William Crookes † and by Dr. H. S. Washington.‡

The silicate is fused with its own weight of pure resublimed ammonium chloride, and six times its weight of pure calcium carbonate prepared by precipitation with ammonium carbonate from a hot solution of the pure chloride, the precipitated calcium carbonate being filtered off, well washed, and dried.

It must be remembered that the silicate forms only a portion of the materials, the analysis of which we are considering, and that a considerable quantity of calcium carbonate is present already. This should be taken into account when calculating the quantities of ammonium chloride and calcium carbonate to be added. Thus in a cement mixture containing, as

* *American Journal of Science*, vol. i., 1871, p. 269.
† *Select Methods in Chemical Analysis*, 1894, p. 26.
‡ *The Chemical Analysis of Rocks.* London, Chapman & Hall, 1904.

it would, about 75 per cent. of carbonate of lime, it would only be necessary to add ammonium chloride, to the extent approximately of one-quarter the weight of the substance taken, and calcium carbonate equal to three-fourths of its weight.

The required quantities of ammonium carbonate and calcium carbonate having been weighed off, they are added to the weighed quantity of the substance in the porcelain mortar, the whole being thoroughly mixed together. The mixture is transferred to a platinum crucible which is heated, at first gently, finally, for an hour to full redness over a blowpipe flame. When cool, the crucible with its contents is placed in a platinum or porcelain dish, water is added, and the contents of dish are heated. The sintered mass, after a short time, becomes detached from the crucible and disintegrates. The contents of the crucible are then washed into the dish. When completely disintegrated, the contents of the dish are filtered, and the precipitate is well washed. The precipitate is rejected, the filtrate contains the alkalies, together with the lime and also magnesia if present, as it generally is in limestones. The liquid is heated, after addition of ammonium hydrate and ammonium carbonate in sufficient quantity to precipitate the whole of the lime, together with a few drops of ammonium oxalate. It is heated, filtered, and the precipitate is well washed. The filtrate and washings are concentrated in a large porcelain dish until ammonia salts begin to crystallise out. The contents of dish are then washed into a wide-mouthed flask of ample capacity, and strong, pure nitric acid is added in sufficient quantity to decompose the ammonia salts present. The flask is heated upon a sand-bath, and the contents are evaporated in the flask to complete dryness. Professor Smith proposes to effect this evaporation in a porcelain dish, after the decomposition in the flask is complete, stating that the dish should be of Berlin porcelain. Our own experience is that the dish is acted upon to a considerable extent by the acid solution, and that the evaporation is best effected in the flask. The residue is boiled with baryta water to remove magnesia, and sulphuric acid if this is present, the precipitate is filtered off, and well washed, the excess of baryta being removed from the filtrate by heating it with ammonium hydrate and carbonate. The precipitate is filtered off and well washed, the filtrate contains the alkalies. It is evaporated to complete dryness in a weighed platinum dish, after the addition of a few drops of hydrochloric acid. The dish is carefully heated on a sand-bath to ensure perfect dryness, and, when cold, is weighed. The mixed chlorides are separated as follows :—

**Separation of the Sodium and Potassium Chlorides.**—The contents of the dish are dissolved in water, a few drops of hydrochloric acid are added, together with platinum chloride solution in excess. The dish is heated on a water-bath until the contents are in a semi-fluid pasty condition, a little (96 per cent.) alcohol is then added, and the dish is gently rotated to mix the

contents. The double salt of platinum and potassium crystallises out as the liquid concentrates on the water-bath. If it becomes colourless, or of a pale straw colour, sufficient platinum chloride solution has not been added. When the precipitate has settled, the supernatant liquid is decanted over a filter that has been previously washed, dried at 100°, and weighed. The treatment with alcohol is repeated once. The precipitate is then washed from the dish upon the filter with a jet of alcohol, contained in a small wash-bottle. It can readily be removed from the dish by this means, and should not be broken up by scrubbing. The washing with alcohol is continued until the washings are colourless. The filter with precipitate is dried at 100°, and weighed. The sodium chloride is taken by difference. Both chlorides are calculated to oxides.

The potash may be determined by the perchloric acid method, which is quite accurate and avoids the use of the now costly platinum salt. After weighing, the mixed chlorides are dissolved in about 20 c.c. of hot water, sufficient (about 1 c.c.) of 60 per cent. perchloric acid to convert both
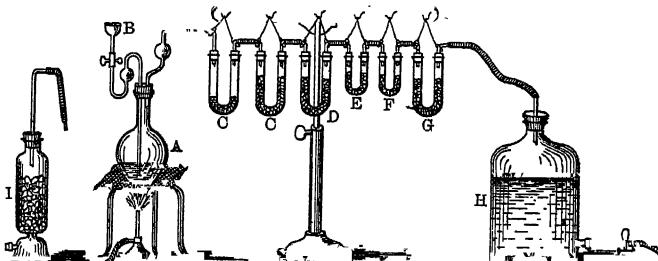


Fig. 2.—Apparatus for Determination of Carbon Dioxide.

chlorides into chlorates is added, the mixture is heated until fumes of perchloric acid are given off, and the operation is repeated. When cool, about 20 c.c. of 96 per cent. alcohol containing 1 per cent. of perchloric acid are added to the contents of dish. Sodium chlorate is soluble in alcohol, while potassium chlorate is not. The precipitate is collected on a weighed filter, washed with the same alcohol, dried at 100°, and weighed as potassium perchlorate, $KClO_4$.

**Quantity No. 5—Determination of Carbon Dioxide.**—This should be determined by the increase in weight of absorption tubes. One of the best forms of apparatus for this purpose is shown by Fig. 2, taken from Sexton's *Outlines of Quantitative Analysis.**

A is the evolution flask holding about 200 c.c. provided with a caoutchouc stopper with two perforations through one of which passes a tube reaching just through the stopper, and through the other a tube reaching nearly

* Charles Griffin & Co., Ltd., London. Fifth Edition, 1907, p. 34.

to the bottom of the flask. This tube is connected with a small funnel B, by means of a short piece of caoutchouc tube which can be securely closed by a pinch cock. C C D are U-tubes, C C contain calcium chloride, D contains copper sulphate on pumice prepared by boiling fragments in a saturated solution of sulphate of copper, and drying and heating them to complete dehydration. E and F are the weighed tubes for the absorption of the carbon dioxide. They are filled, the first three-fourths of each with coarse granulated soda lime, the last quarter with calcium chloride. G is filled with calcium chloride to prevent access of moisture. H is a large tubulated bottle to serve as an aspirator. I is a tube of soda lime to remove carbon dioxide from air which has to be aspirated through the apparatus after the flask A has been disconnected. All the chloride of calcium should be free from alkaline reaction. To ensure this, fill a number of U-tubes with granular calcium chloride, suspend them in series and aspirate a current of dry carbon dioxide through them. The U-tubes used in this apparatus should be fitted with caoutchouc stoppers, but those with glass stoppers and leading tubes are more convenient.

To make the determination, add a little water to the weighed quantity of the substance in the flask A, connect the various parts of the apparatus, making sure that the connections are secure, and fill the funnel B with dilute hydrochloric acid. Open the pinch cock and allow a little acid to enter the flask, continuing gently until decomposition is complete. Close the pinch cock, remove the funnel B, connect the caoutchouc tube with the tube from I, aspirate a gentle current of air through the apparatus, cautiously heating the contents of flask to incipient ebullition. Continue the aspiration until the soda lime tubes become cold. They are then disconnected and weighed. The ends of the connecting tubes should be closed with stoppers of glass rod while weighing, both before and after the operation. With stoppered tubes it is only necessary to turn the stoppers a sufficient distance to close the leading tubes.

**The Analysis of Clay and Shale** — *Classification.* — For the purpose of analysis, clay and shale may be divided into three classes.

1. That in which calcium carbonate is absent, or in which it occurs in small or very moderate quantity.

2. That in which calcium carbonate is present in quantity reaching 40 or 50 per cent., as, for instance, in gault clay, the clays and shales of the lias, and the shales of the carboniferous limestone formation.

3. Alluvial mud from the banks of tidal rivers, such as Medway mud, in which calcium carbonate is either absent or present in small quantity, but which may contain chlorides and sulphates of magnesium, and of the alkali metals.

## 1. Analysis of Clay or Shale containing Calcium Carbonate in Small Quantity.

**Determination of Silica, Alumina, Oxide of Iron, Lime, and Magnesia.**— From the weighing tube a quantity of about ·75 gramme is transferred to a platinum crucible, and fused with six times its weight of fusion mixture or pure dry sodium carbonate. Some text-books advise the use of a larger quantity than this, which is doubtless necessary for certain silicates, but our own experience shows that any silicates occurring in cement materials are entirely broken up by fusion with this quantity, and it is always advisable to introduce as little foreign matter as possible into the substance under analysis. The contents of the crucible are fused, the fused mass is extracted with water, and dilute hydrochloric acid in slight excess, heated to expel carbon dioxide, and evaporated to complete dryness in a platinum dish. The silica, oxide of iron, alumina, lime, and magnesia are determined as in limestone.

**Sulphate and Sulphide Sulphur.**—Are determined as in limestone in quantities of about ·75 gramme.

**Potash and Soda.**—These are determined by the method given for limestone, taking about 1 gramme of the substance, decomposing it with the full quantity of the reagents—its own weight of pure resublimed ammonium chloride and six times its weight of pure calcium carbonate.

**Decomposition of Silicates by Hydrofluoric Acid.**—We have employed this method when determining alkalies if a sufficiently strong blast has not been available for the fusion.

The weighed quantity is transferred to a platinum dish cautiously heated with a little pure hydrofluoric acid and a few drops of sulphuric acid sufficient to convert all the bases present into sulphates, evaporated nearly to dryness, and the operation is repeated. The second evaporation should be carried nearly—but not to actual—dryness. The silica is volatilised as silicon fluoride, and the operation must be entirely conducted in the open air, or the windows and all glass apparatus in the laboratory will be attacked. The residue is moistened with concentrated hydrochloric acid, and is set aside for an hour, water is then added, and the dish gently heated. The result should be a clear fluid which is treated exactly as in the case of the filtrate from the sintered mass obtained by the Laurence Smith method. If preferred, fluoride of ammonium may be used for the decomposition, instead of hydrofluoric acid.

**Carbon Dioxide.**—This is determined in the same manner as in limestone.

**Sand.**—It has been previously stated that the silica in Portland cement raw materials may be present in the insoluble condition if it is in a very fine state of division. It may, however, sometimes be desired to determine its quantity, which may be done in the following manner :—

About 1·5 gramme of the dry clay is weighed off and transferred to a platinum dish. Sulphuric acid diluted with its own volume of water is added, the contents of dish are strongly heated for about nine hours, then evaporated until nearly the whole of the sulphuric acid is expelled, freely diluted with water, heated, filtered, and the residue well washed with hot water. It is washed from the filter into the platinum dish, and heated to boiling for a little time with a strong solution of sodium carbonate. The contents of dish are allowed to settle for a minute or two, after which the clear liquid is decanted over a filter. The residue is again treated in the same manner with sodium carbonate solution, and the operation is repeated until it does not appear to decrease in bulk. The filter is kept well washed with hot water, and it is by preference enclosed in a hot water jacket. The contents of dish are finally transferred to the filter and repeatedly washed with hot water. If the washing proceeds slowly, it is probable that the solution while filtering has deposited silica in the gelatinous state upon the filter. In this case, the residue should be washed out of·the filter into the platinum dish, and again boiled with solution of sodium carbonate. It is always safest to pursue this course as the dissolved silica has a great tendency to separate as the solution cools. The residue is returned to the filter, and repeatedly washed with hot water, then with water slightly acidulated with hydrochloric acid, finally with pure hot water. It consists of sand which is ignited in a platinum crucible, and weighed. It may be pure quartz sand, or a mixture of this and a disintegrated silicate such as felspar or mica. Its nature may be determined by fusing it with six times its weight of fusion mixture, separating the silica as directed for the original clay, and determining bases if present, in the filtrate. Free soluble silica, which in clay seldom exceeds 1 per cent., is estimated by extracting about 2 grammes of the original clay by boiling with strong solution of sodium carbonate, filtering, and determining the silica in the filtrate by evaporation with excess of hydrochloric acid in the manner already described.

**Combined Water and Organic Matter.**—For practical purposes, these may be determined by the loss on ignition of about 1 gramme of the material. If the only volatile matters present are water and organic matter, the loss after strong ignition may be so stated. If the material under examination contains other volatile constituents, or those that undergo change when ignited, it is obvious that this result is not the true one. Many clays and shales contain iron sulphide, which during ignition changes to ferric oxide, the sulphur being volatilised. A correction may be made for this by adding to the percentage of loss the percentage of iron sulphide found by analysis, and deducting its equivalent of ferric oxide. If the material contains carbonates, and the percentage of carbon dioxide is known, this may be deducted from the percentage of loss, but obviously care must be taken that all the carbon dioxide is expelled by the ignition. If carbon dioxide is present, the

following method may be adopted.  About 1 gramme of the dried clay is treated in a beaker or evaporating dish with water and dilute hydrochloric acid in very slight excess, it is warmed gently to expel carbon dioxide rendered slightly alkaline with ammonium hydrate, heated to boiling, and filtered through a filter paper that has been previously dried at 105°, and weighed. The residue on the filter is well washed, dried for two hours at 105°, and weighed.  The result, after deducting the weight of the filter paper, is the weight of the true clay, which is strongly ignited with the filter.  The loss is water and organic matter.  If necessary, the correction is made for iron sulphide.

## 2. The Analysis of Clay, Shale, or Marl containing Calcium Carbonate in Considerable Quantity.

About 8 grammes of the dry material are weighed off, and digested with water and dilute hydrochloric acid in very slight excess, heated to expel carbon dioxide, and filtered through a filter paper that has been previously dried at 105°, and weighed.  The residue is well washed, dried with the filter at 105° to constant weight.  Its weight less that of the filter paper is that of the true clay in the quantity taken.  It is removed from the filter paper, finely powdered in an agate mortar, and preserved in a stoppered weighing tube.  Its analysis is made as described under Clay 1, omitting the determination of sulphur as sulphate, which will be found in the hydrochloric acid solution.  The carbon dioxide is determined in about 1 gramme of the original material.  Weighed quantities of from ·75 to 1 gramme of the separated clay are taken for the determination of silica, alumina, oxide of iron, lime, and magnesia, for sulphide of iron if present, for potash and soda, for sand if it is desired to determine this, and for water and organic matter. The filtrate from the clay is made up to 500 c.c., 100 c.c. are taken for the estimation of silica, alumina, oxide of iron, lime and magnesia, and 100 c.c. for sulphuric acid.

## 3. Analysis of Medway or Salt Water Mud.

This may be analysed by the first method given for clay.  The analysis of Gillingham mud given in the next chapter was made by the following method, which may be employed if a more detailed examination is required. This analysis should be referred to as regards the arrangement of results.

About 8 grammes of the dried mud are weighed off, digested with water and dilute nitric acid, heated, filtered, well washed, dried at 105°, and weighed, exactly as in Clay 2.  Note that nitric acid, and not hydrochloric acid, is used for the separation.  The clay is separated from the filter paper, finely powdered, and preserved in a stoppered tube.  Sand, silica, alumina, oxide of iron, lime and magnesia, potash and soda, and water and organic matter,

are estimated in portions of from ·75 to 1 gramme, as in the case of Clay 2. Carbon dioxide, if present, is determined in about 3 grammes of the original material.

The filtrate from the clay is made up to 1 litre. 250 c.c. are taken for the determination of potash and soda. This is treated exactly as in the filtrate from the sintered mass obtained in the first stage of the Laurence Smith method, as described in the analysis of limestone. Silica, alumina, oxide of iron, lime and magnesia, are determined in 200 c.c. of the solution, sulphuric acid in 200 c.c. 200 c.c. are rendered neutral, or very faintly alkaline, with sodium carbonate, a few drops of potassium chromate solution are added, and the chlorine is determined by titration with standard silver nitrate.

### The Analysis of Portland Cement.

A perfect method of cement analysis has yet to be devised. In the present state of our knowledge we can only make an ultimate analysis determining the percentage of each constituent. They undoubtedly exist in combination, but no method of proximate analysis has yet been devised by which these combinations may be separated and determined.

Taken alone, the analysis of Portland cement gives no indication of its quality. It may agree in ultimate composition with cement that has been proved to be of the highest quality, and yet itself be faulty. Chemical analysis will show if it has been made from suitable materials, if they occur in the correct proportions, and if certain constituents, such as magnesia or sulphuric acid, excess of which would be likely to give trouble, are within the proper or the required limits. It is also possible by this means to detect most forms of adulteration. The analysis will not show if the constituents of the raw mixture, although they may be in the correct proportions, have been properly ground or uniformly mixed, or even if the cement has been sufficiently burned. To determine these points, and to obtain complete information as to the properties of Portland cement, recourse must be had to mechanical tests, in addition to chemical analysis.

**Sampling.**—The method of sampling from bulk will be described in a later chapter, when dealing with mechanical tests. A fraction of this sample is taken for analysis, it is not necessary to grind it finer. Samples of clinker for analysis should be broken down and prepared as described for limestone, the final grinding being about as fine as that of ordinary cement. Samples should be preserved in closely stoppered bottles, and weighed from a stoppered tube.

**Determination of Silica, Oxides of Iron and Alumina, Lime and Magnesia.** —These are determined exactly as in the case of limestone, or the mixture of raw materials in from ·5 to ·75 gramme of the cement. Previous fusion

is not necessary, as the active silica separates entirely as a gelatinous hydrate on heating and digesting the cement with hydrochloric acid. Before adding the acid, the weighed quantity should be triturated with a little water until all tendency to set has disappeared.

**Determination of Insoluble Residue and Sulphuric Acid.**—In all cements a small portion of what separates as silica is insoluble in a boiling solution of sodium carbonate, and is consequently inactive. It is probably in greater part derived from the ash of the fuel. In analysis results it is generally described as insoluble residue, and in cements of good quality it rarely exceeds from 1 to 2 per cent. A quantity of about ·75 gramme of cement is weighed off, and the silica is separated as previously described, but the second evaporation is not necessary.

Sulphuric acid is determined in the filtrate by precipitation with barium chloride. The silica is washed out of the filter into a platinum dish, and the insoluble portion is determined by boiling with solution of sodium carbonate, as described under the analysis of sand. The percentage found is deducted from that of the total silica.

**Determination of Total Iron.**—The filtrate from the barium sulphate may be conveniently used for this determination, and the troublesome fusion of the ignited oxides of iron and aluminium is thus avoided. The solution is rendered slightly alkaline with ammonium hydrate, heated to boiling, the precipitate is filtered off, and well washed. It is dissolved in a little dilute sulphuric acid, the iron is reduced by zinc or hydrogen sulphide, and the solution is titrated with standard permanganate, or the precipitate may be dissolved in hydrochloric acid, the iron reduced, and the solution titrated with standard bichromate. If desired, the iron may be determined gravimetrically. The mixed oxides are dissolved in the smallest possible quantity of hydrochloric acid, and the ferric oxide separated from the solution by caustic soda, by the method described under the analysis of limestone. The iron may, if desired, be determined in a portion of the original cement. About 1 gramme is taken, boiled with dilute hydrochloric acid until decomposed, the iron is reduced, and the solution titrated with standard bichromate. If it is preferred to use permanganate, the hydrochloric acid solution is rendered slightly alkaline with ammonium hydrate, boiled, the precipitate filtered off, well washed, dissolved in dilute sulphuric acid, the iron reduced, and the solution titrated.

**Determination of Ferrous Iron.**—This is generally present in cement in very small quantity. To estimate it, from 4 to 5 grammes of cement is triturated in an evaporating dish with an excess of water until all tendency to set has disappeared, and a little sodium bicarbonate is then added. The mixture is washed into a flask fitted with a doubly bored stopper, through one hole of which passes a funnel or thistle-headed tube with stopcock, through the other a tube fitted with a Bunsen valve. The cement is de-

composed by heating with dilute hydrochloric acid, which is admitted to the flask by the funnel tube, and the ferrous iron is determined by titration with standard bichromate.

**Determination of Sulphide Sulphur.**—About 5 grammes are taken for the determination of sulphur existing, combined with calcium, as calcium sulphide. The weighed quantity is triturated with excess of water in a porcelain dish to a thin slip, and is then washed into a flask fitted with a doubly bored rubber stopper. A funnel or a thistle-headed tube with stop-cock passes through one of the holes and reaches nearly to the bottom of the flask, one limb of a tube bent twice at right angles is inserted in the other hole, reaching only just through the stopper. The other limb dips into a solution of cadmium chloride contained in a narrow, deep beaker or a cylinder such as a Nessler glass. It should reach nearly to the bottom of the vessel. Dilute hydrochloric acid is passed through the funnel tube into the flask, which is gently heated until the cement is entirely decomposed, the contents being finally boiled. The contents of the beaker or cylinder are passed over a filter that has been previously washed, dried at 100°, and weighed. The precipitate of cadmium sulphide is washed, dried on the filter at 100°, and weighed, the per cent. of calcium sulphide being calculated from the weight of the cadmium sulphide.

**Potash and Soda.**—These are determined as described in the analysis of limestone. Fusion of the cement is not necessary, as the silicates have been broken up, and the alkalies separated during its calcination. About 1 gramme is taken for the determination. The silica is separated in the manner already described, the second evaporation is not necessary. The filtrate from this operation is treated exactly as that from the fused mass obtained by the Laurence Smith process. It may seem that as the silica in a hydrochloric acid solution is precipitated on the addition of ammonium hydrate it is unnecessary to separate it. But it forms a very voluminous gelatinous precipitate requiring persistent washing to ensure the entire removal of the alkali salts, and it is best got rid of at the commencement.

**Loss on Ignition.**—A quantity of about 1 gramme is heated to a low cherry-red heat in a platinum crucible to constant weight. The loss, generally described in analysis results as "loss on ignition," is considered to be carbon dioxide and water. An extreme temperature should not be employed for the ignition, as it involves risk of loss by volatilisation of sulphuric acid, which thus causes the true loss to come out too high.

## The Analysis of Lime.

Hydraulic lime may be analysed by the method given for Portland cement. With pure or comparatively pure limes, the method adopted must depend upon what is required to be known regarding them. Frequently,

a determination of lime alone, or of lime and magnesia, is all that is needed. A quantity of about ·5 gramme is dissolved in dilute hydrochloric acid, the solution is rendered slightly alkaline with ammonium hydrate, heated to boiling, and the precipitate of silica and the oxides of iron and aluminium filtered off, ignited, and weighed. Lime and magnesia are determined in the filtrate. The loss on ignition should not be omitted in an analysis of lime, and, except in the case of selenitic lime, it may be made at a higher temperature then in cement. By determining also the carbon dioxide, the actual lime, and that present as carbonate and as hydrate, may be stated in the results. If it is required to determine the silica and the oxides of iron and aluminium separately, 2 grammes should be taken for the analysis, and these constituents separated as in Portland cement. The filtrate from the iron and alumina is made up to 1 litre, 250 c.c. are taken for the estimation of lime and magnesia, and 500 c.c. for sulphuric acid.

### Determination of Lime by Titration with Potassium Permanganate.

A determination of lime only is sometimes necessary, and it may be made in the following manner :—Of limestone or raw mixture about ·3 gramme is taken, of lime or cement about ·2 gramme. The weighed quantity is transferred to a beaker, treated with dilute hydrochloric acid, boiled, rendered slightly alkaline with ammonium hydrate, and heated to boiling, the solution is decanted over a filter, and the precipitate washed twice by decantation. It is heated with a little dilute hydrochloric acid, rendered slightly alkaline with ammonium hydrate, heated to boiling, transferred to filter previously used, and the precipitate washed until free from lime. The lime is determined in the filtrate, the clay may be ignited, and weighed. The estimation of clay is a valuable guide to the accuracy of cement mixtures. Indeed, in some French works we believe it is the only method employed for this purpose. If the clay falls below 20 per cent. the mixture is either over basic or dangerously near the limit of safety.

The filtrate is heated to boiling, boiling solution of ammonium oxalate is added in sufficient excess, and the boiling continued for two minutes. The calcium oxalate separates as a granular precipitate, which rapidly settles from the liquid. The beaker is cooled by immersion in water, the clear liquid is decanted over a filter, and the precipitate is washed by decantation until it is free from ammonium oxalate, about eight washings are usually sufficient. The washing is continued until a little of the filtrate, after boiling with a few drops of calcium chloride, gives neither precipitate nor cloudiness. The filter paper is opened out on a flat-bottomed dish of slightly larger diameter, and the adhering precipitate is washed into the beaker containing the main quantity. It is then covered with a little dilute—1 to 10—sulphuric acid, gently warmed, the acid solution transferred to the beaker, and the

paper thoroughly washed with hot water. This treatment should not be omitted, as calcium oxalate is retained in the pores of the paper, and is not removed by simple washing. Dilute sulphuric acid is added to the contents of beaker, the solution is heated to from 70° to 80°, and titrated with deci-normal permanganate until a faint pink colour diffuses through the liquid. The permanganate solution should be standardised on pure calcium carbonate. Two quantities of about ·2 gramme each are weighed off, transferred to beakers, dissolved in dilute hydrochloric acid, boiled to expel carbon dioxide, rendered slightly alkaline with ammonium hydrate, the solution boiled, and the lime precipitated in the boiling solution by a boiling solution of ammonium oxalate. The remainder of the operation is exactly as just given for the determination of lime by titration with permanganate. The mean of the two determinations is taken as the result. As the salt is not easy to obtain pure and of normal composition, the solution is not likely to be strictly deci-normal. By dividing the weight of each quantity of calcium carbonate taken by the number of c.c. of the solution it required, and taking the mean of the two results, the calcium carbonate value of 1 c.c. is obtained. This number multiplied by ·56 gives the lime value. The solution should be kept in the dark, and occasionally re-standardised.

**Determination of Lime without Separation of the Clay.**—This method is given by Richard K. Meade.* It is quite as accurate as the one last given, is more rapid, and may be used if a determination of the clay is not required. About ·3 gramme of the sample is weighed off, transferred to a beaker, and boiled with dilute hydrochloric acid until decomposition is complete. Ammonium hydrate is cautiously added until a slight permanent precipitate is formed, and then 10 c.c. of a 10 per cent. solution of oxalic acid is added. This method depends on the fact that the oxides of iron and aluminium are soluble in oxalic acid, and that calcium oxalate is not. The mixture is stirred until these oxides are entirely dissolved, the solution is made up to about 200 c.c., boiled, and sufficient boiling saturated solution of ammonium oxalate is added to precipitate the lime, the boiling is continued for one or two minutes. The solution is cooled by immersing the beaker in water, filtered, and the precipitate is treated in the same manner as the clean oxalate precipitate obtained in the case of the separation of the clay, titrating with deci-normal permanganate. When employing this method for cement, the original solution should be boiled with a little bromine water, or a few drops of strong nitric acid, to oxidise any ferrous oxide or calcium sulphide present which would reduce the permanganate and give too high results. For the same reason, the weighed quantity of raw material, or limestone, should be strongly ignited over a blast lamp for a few minutes to destroy organic matter.

The determination of lime by titration with permanganate gives very

* *Portland Cement.* The Chemical Publishing Co., Easton, Pa., 1906.

accurate results, quite as accurate as those obtained by gravimetric methods. With a sample of cement raw mixture the following results were obtained :—

1. The lime weighed as carbonate, .     .     .     74·99 per cent. CaCO₃.
2. By titration with permanganate, clay
   separated,     .     .     .     .     .     .     75·09      ,,
3. By the R. K. Meade method,     .     .     .     75·05      ,,

## The Analysis of Plaster of Paris and Gypsum.

**Determination of Insoluble Residue, Lime, and Sulphuric Acid.**—The material is finely powdered, a weighed quantity of about 1·5 gramme is transferred to a beaker, boiled with dilute hydrochloric acid until decomposed, rendered slightly alkaline with ammonium hydrate, again boiled, filtered, and washed. Unless in very small quantity, the residue is washed out of the filter after two washings, heated with a little dilute hydrochloric acid, rendered slightly alkaline with ammonium hydrate, again boiled, the precipitate returned to the filter, washed, and ignited. It is reported as insoluble residue. It is probably clay and, if desired to determine its nature, it is fused with six times its weight of fusion mixture, the silica separated in the manner already described, and the oxides of iron and aluminium determined in the filtrate. The filtrate from the insoluble matter is made up to 1 litre, 300 c.c. are taken for the estimation of lime, and 300 c.c. for sulphuric acid.

**Determination of Water.**—A weighed quantity of about 1 gramme is heated in a platinum crucible at a temperature of 100° to constant weight. The loss is hygroscopic water. The crucible is now heated for 30 minutes over a Bunsen burner at a low cherry-red heat, cooled, and weighed. The loss is combined water. It is possible that during ignition some sulphuric acid has been lost by volatilisation. The contents of crucible are transferred to a beaker, and the insoluble matter separated as before directed. The filtrate is made up to 1 litre, and 500 c.c. are taken in which the sulphuric acid is determined. If the percentage found here is less than the percentage found in the other determination, loss has occurred. If this is so, the difference between the two percentages deducted from the percentage of loss by ignition gives the correct figure for combined water.

The value of gypsum when used for grinding with the clinker to regulate the setting time of the cement depends upon the amount, or the number of units of sulphuric acid it contains. To determine this a full analysis is not necessary. The sample is finely powdered, about ·3 gramme is weighed off, decomposed with hydrochloric acid, boiled, and the insoluble matter filtered off, and well washed. The sulphuric acid is determined in the filtrate. The percentage is calculated on the gypsum as received for use, including both the hygroscopic water, and the insoluble matter.

## Cement Adulteration.

**Detection of Adulteration.**—The admixture of Portland cement with less valuable materials is not commonly practised in this country. Attention was first called to the subject in 1894, when certain manufacturers in the London district were found to be grinding Kentish rag—a siliceous limestone —with their clinker. The practice in question is, however, of much older date than this. So far back as 1871, John Glover, the inventor of the Glover Tower, so well known in the alkali industry, read a paper before the Chemical Society of Newcastle-upon-Tyne on " The Adulteration of Portland Cement with Slags." In 1882, attention was called to the subject at a meeting of the German Society of Cement Manufacturers, and it was declared to be a fraud upon the purchaser. Experiments were undertaken by Messrs. R. and W. Fresenius at the request of the Society,* and certain rules for its detection were laid down. The subject was investigated in this country by Messrs. Stanger and Blount, with special reference to the addition of Kentish rag.

The choice of materials for this purpose is necessarily limited, as they must be of low cost, and they must not affect the colour of the cement. Among possible ingredients are certain limestones, sandstones, old firebricks, hard shales, and blast-furnace slag. The addition of sandstone, siliceous limestone, shale, or firebrick is easily detected by the determination of insoluble residue. This, in a normal cement, does not exceed 2 per cent., and is generally less. If higher than 2 per cent., the addition of some siliceous substance may be taken for granted.

The loss on ignition in well-burned and matured cement rarely exceeds 2·5 per cent. If limestone has been added, it will certainly be greater than this, while the addition of an impure limestone will also result in a high percentage of insoluble residue.

Adulteration by blast-furnace slag is not easily detected, as many slags approach very closely in their composition to that of Portland cement. Owing to the presence of sulphur, as sulphide, and ferrous iron, Messrs. Fresenius found that the reducing action of slags, when titrated with potassium permanganate, was much greater than that of pure Portland cement. Of 12 samples of pure cements experimented upon, the quantity of permanganate, reduced by 0·1 gramme, varied from 0·79 to 2·8 milligrammes; of five samples of slag, from 44·34 to 74·6 milligrammes. From these results they say that the weight of permanganate, reduced by 1 gramme of cement, should not exceed 2·8 milligrammes. This is disputed by Dr. Michaelis,† who experimented with five samples of pure cement. No. 1 required 11·6, No. 2 3·3, No. 3 19·9, No. 4 14·7, and No. 5 1·2 milligrammes of permanganate. The Fresenius test would condemn all these cements except the last.

* *Zeitschrift für analytische Chemie*, vol. xxiii., p. 175.
† *Thonind. Zeit.*, vol. xxiv. (59), p. 860.

FACTORS FOR USE IN CEMENT ANALYSIS WITH THEIR LOGARITHMS.
*Calculated from the Atomic Weights in the International Table—*H = 1.

| Found. | Sought. | Factor. | Logarithm. |
|--------|---------|---------|------------|
| $BaSO_4$ | $CaSO_4$ | ·5831 | $\overline{1}$·7657430 |
| $BaSO_4$ | $CaSO_4 2H_2O$ | ·7374 | $\overline{1}$·8677031 |
| $BaSO_4$ | S | ·1373 | $\overline{1}$·1376705 |
| $BaSO_4$ | $SO_3$ | ·3429 | $\overline{1}$·5351675 |
| $BaSO_4$ | $H_2SO_4$ | ·4206 | $\overline{1}$·6238693 |
| $2BaSO_4$ | $FeS_2$ | ·2570 | $\overline{1}$·4099331 |
| | | | |
| CdS | CaS | ·4994 | $\overline{1}$·6984485 |
| CdS | S | ·2219 | $\overline{1}$·3461573 |
| CdS | $CaSO_4$ | ·9422 | $\overline{1}$·9741431 |
| | | | |
| CaO | $CaCO_3$ | 1·7843 | 0·2514679 |
| CaO | $CaSO_4$ | 2·4272 | 0·3851056 |
| CaO | $CaSO_4 2H_2O$ | 3·0695 | 0·4860676 |
| CaO | $CaOH_2O$ | 1·3211 | 0·1209357 |
| $CaCO_3$ | CaO | ·5604 | $\overline{1}$·7484981 |
| $CaCO_3$ | $CaSO_4$ | 1·3603 | 0·1336347 |
| $CaCO_3$ | $CaSO_4 2H_2O$ | 1·7202 | 0·2355789 |
| $CaCO_3$ | $CO_2$ | ·4395 | $\overline{1}$·6429589 |
| $CO_2$ | $CaCO_3$ | 2·2750 | 0·3569814 |
| $CaSO_4$ | $CaSO_4 2H_2O$ | 1·2645 | 0·1019188 |
| $CaSO_4$ | $SO_3$ | ·5880 | $\overline{1}$·7693773 |
| $SO_3$ | $CaSO_4$ | 1·7006 | 0·2306022 |
| $CaOH_2O$ | CaO | ·7569 | $\overline{1}$·8790385 |
| | | | |
| $Fe_2O_3$ | $2FeO$ | ·8999 | $\overline{1}$·9541943 |
| $2FeO$ | $Fe_2O_3$ | 1·1112 | 0·0457922 |
| $Fe_2O_3$ | $2FeS_2$ | 1·5022 | 0·1767278 |
| $FeS_2$ | $Fe_2O_3$ | ·6656 | $\overline{1}$·8232133 |
| $FeS_2$ | Fe | ·4657 | $\overline{1}$·6681062 |
| $FeS_2$ | $S_2$ | ·5342 | $\overline{1}$·7277039 |
| | | | |
| MgO | $MgCO_3$ | 2·0901 | 0·3201671 |
| $MgCO_3$ | MgO | ·4784 | $\overline{1}$·6797912 |
| $Mg_2P_2O_7$ | $2MgO$ | ·3624 | $\overline{1}$·5591882 |
| $Mg_2P_2O_7$ | $2MgCO_3$ | ·7575 | $\overline{1}$·8793826 |
| | | | |
| $K_2PtCl_6$ | $2KCl$ | ·3071 | $\overline{1}$·4872798 |
| $K_2PtCl_6$ | $K_2O$ | ·1941 | $\overline{1}$·2880255 |
| $2KCl$ | $K_2O$ | ·6320 | $\overline{1}$·8007171 |
| | | | |
| $2NaCl$ | $Na_2O$ | ·5308 | $\overline{1}$·7249309 |

*From the Table of International Atomic Weights.*

| | | O = 16. | H = 1. | | | O = 16 | H = 1. |
|---|---|---|---|---|---|---|---|
| Aluminium,. . | Al | 27·1 | 26·9 | Lead, . . . . | Pb | 206·9 | 205·35 |
| Antimony, . . | Sb | 120·2 | 119·3 | Lithium, . . . | Li | 7·03 | 6·98 |
| Arsenic, . . . | As | 75·0 | 74·4 | Magnesium, . | Mg | 24·36 | 24·18 |
| Barium, . . . | Ba | 137·4 | 136·4 | Manganese, . . | Mn | 55·0 | 54·6 |
| Bismuth,. . . | Bi | 208·5 | 206·9 | Mercury, . . | Hg | 200·0 | 198·5 |
| Boron, . . . | B | 11 | 10·9 | Nickel, . . . | Ni | 58·7 | 58·3 |
| Bromine,. . . | Br | 79·96 | 79·36 | Nitrogen, . . | N | 14·04 | 13·93 |
| Cadmium, . . | Cd | 112·4 | 111·6 | Oxygen, . . . | O | 16·00 | 15·88 |
| Calcium, . . . | Ca | 40·1 | 39·8 | Phosphorus, . | P | 31·0 | 30·77 |
| Carbon, . . . | C | 12·00 | 11·91 | Platinum, . . | Pt | 194·8 | 193·3 |
| Chlorine,. . . | Cl | 35·45 | 35·18 | Potassium, . . | K | 39·15 | 38·86 |
| Chromium, . . | Cr | 52·1 | 51·7 | Silicon, . . . | Si | 28·4 | 28·2 |
| Cobalt, . . . | Co | 59·0 | 58·56 | Silver, . . . | Ag | 107·93 | 107·12 |
| Copper, . . . | Cu | 63·6 | 63·1 | Sodium, . . . | Na | 23·05 | 22·88 |
| Fluorine, . . | F | 19 | 18·9 | Strontium, . . | Sr | 87·6 | 86·94 |
| Gold, . . . . | Au | 197·2 | 195·7 | Sulphur, . . . | S | 32·06 | 31·83 |
| Hydrogen, . . | H | 1·008 | 1·000 | Tin, . . . | Sn | 119·0 | 118·1 |
| Iodine, . . . | I | 126·85 | 125·90 | Titanium, . . | Ti | 48·1 | 47·7 |
| Iron, . . . . | Fe | 55·9 | 55·5 | Zinc, . . . . | Zn | 65·4 | 64·9 |

# CHAPTER VIII.

## ANALYSES OF RAW MATERIALS AND PORTLAND CEMENT, CALCULA-TION OF PROPORTIONS, RAPID METHODS OF ANALYSIS, SPECIFIC GRAVITY.

CONTENTS.—Analyses of Raw Materials, Portland Cement and Clinker—Calculations of Proportion of Raw Materials and Rapid Methods of Testing their Accuracy—Calcimeters—The Lunge Nitrometer—Testing the Fineness of Raw Flour and Slurry—Specific Gravity.

**Analyses of Raw Materials.**—The analyses which follow have been selected from among others, made by the authors, as being fairly representative of materials either generally employed in, or suitable for, the manufacture of Portland cement. The uncombined silica has not, in every case, been determined, as modern practice conclusively shows, as we have previously explained, that if the mixture with carbonate of lime is suitably proportioned, and ground sufficiently fine, sandy clays, or those in which much of the silica occurs uncombined in the insoluble form, may be successfully used, as it is brought into the soluble form during the process of burning. Analyses of lias limestone and lime have been given in an earlier chapter.

### Gault Clay.

*No. 1 from Arlesey, Herts; No. 2 from Sussex.*

|  | No. 1. | No. 2. |
|---|---|---|
| Silica (as fine sand), | 12·28 | 16·35 |
| Silica, combined, | 27·53 | 28·08 |
| Oxide of iron, | 5·70 | 7·47 |
| Alumina, | 13·94 | 15·08 |
| Lime, | 1·18 | 1·08 |
| Magnesia, | 1·17 | ·90· |
| Carbonate of lime, | 30·73 | 21·52 |
| Carbonate of magnesia, | 1·38 | 1·10 |
| Sulphate of lime, | ·52 | 1·96 |
| Combined water and organic matter, | 5·02 | 5·80 |
| Potash and soda (not determined), | ·· | ·· |
|  | 99·45 | 99·34 |

## Medway Mud.

### *From Gillingham.*

| | | |
|---|---:|---|
| Silica, . . . . . | 38·413 | ⎤ As sand in an extremely |
| Alumina, with traces of iron, . . | 1·856 | ⎦ fine state of division. |
| Silica, . . . . . . | 25·249 | ⎫ |
| Alumina, . . . . . . | 14·244 | ⎪ |
| Oxide of iron, . . . . . | 6·774 | ⎪ |
| Lime, . . . . . . | ·810 | ⎬ Combined as silicates. |
| Magnesia, . . . . . | 1·727 | ⎪ |
| Potash, . . . . . . | 2·957 | ⎪ |
| Soda, . . . . . . | ·773 | ⎪ |
| Water, . . . . . . | 3·384 | ⎭ |
| Iron pyrites, . . . . . | ·214 | |
| Silica, . . . . . . | ·118 | |
| Oxide of iron, with trace of oxide of | | |
| manganese, . . . . | ·214 | |
| Alumina, . . . . . . | ·123 | |
| Calcium sulphate, . . . . | ·490 | |
| Magnesium sulphate, . . . . | ·425 | |
| Magnesium chloride, . . . . | ·024 | |
| Potassium chloride, . . . . | ·524 | |
| Sodium chloride, . . . . | 2·166 | |

100·455

## Alluvial Clay.

### *North of England.*

| | |
|---|---:|
| Silica (as fine sand), . . . . . . . . | 41·84 |
| Silica, combined, . . . . . . . . | 24·22 |
| Oxide of iron, . . . . . . . . . | 6·80 |
| Alumina, . . . . . . . . . | 15·00 |
| Lime, . . . . . . . . . | 1·66 |
| Magnesia, . . . . . . . . . | 1·43 |
| Sulphate of lime, . . . . . . . . | ·19 |
| Combined water and organic matter, . . . . . | 7·95 |
| Potash and soda (not determined), . . . . . | .. |

99·09

## Boulder Clay.

### *From the Tyne.*

| | |
|---|---:|
| Silica (as fine sand), . . . . . . . . | 14·56 |
| Silica, combined, . . . . . . . . | 41·43 |
| Oxide of iron, . . . . . . . . . | 10·66 |
| Alumina, . . . . . . . . . | 15·81 |
| Lime, . . . . . . . . . | 3·00 |
| Magnesia, . . . . . . . . . | 2·16 |
| Sulphate of lime, . . . . . . . . | ·15 |
| Combined water and organic matter, . . . . . | 10·64 |
| Potash and soda (not determined), . . . . . | .. |

98·41

RESULTS OF ANALYSES OF CHALK AND LIMESTONE.

| | No. 1. | No. 2. | No. 3. | No. 4. | No. 5. | No. 6. | No. 7. | No. 8. | No. 9. |
|---|---|---|---|---|---|---|---|---|---|
| Silica, | ·84 | 3·43 | 7·98 | ·93 | 7·70 | 2·15 | 2·27 | 1·25 | 15·28 |
| Alumina, | ·23 | 1·73 | 2·86 | ·25 | 1·23 | ·27 | 1·46 | ·32 | 4·50 |
| Oxide of iron, | ·09 | 1·02 | 1·31 | ·32 | 1·65 | ·42 | ·79 | ·21 | 1·61 |
| Iron pyrites, | .. | .. | .. | .. | .. | .. | .. | ·13 | .. |
| Sulphate of lime, | .. | .. | .. | .. | .. | .. | ·23 | .. | .. |
| Carbonate of lime, | 98·37 | 92·98 | 86·45 | 97·87 | 87·36 | 95·97 | 93·47 | 95·04 | 71·21 |
| Carbonate of magnesia, | ·21 | ·49 | ·64 | ·45 | 1·92 | 1·41 | 1·42 | 2·54 | 5·67 |
| | 99·74 | 99·65 | 99·24 | 99·82 | 99·86 | 100·22 | 99·64 | 99·49 | 89·27 |

## Shales.

*No.* 1, *Carboniferous, South of Ireland; No.* 2, *Silurian, South of Ireland.*

|  | No. 1. | No. 2. |
|---|---|---|
| Silica, | 64·05 | 69·00 |
| Oxide of iron, | 8·04 | 8·50 |
| Alumina, | 16·06 | 16·07 |
| Lime, | 1·00 | ·35 |
| Magnesia, | 1·58 | 2·15 |
| Potash, | 3·44 | * |
| Soda, | 1·61 | * |
| Loss on ignition, | 4·29 | 3·07 |
|  | 100·07 | 99·14 |

* Not Determined.

## Chalk and Limestone.

No. 1. Upper or white chalk,    .    Kent, England.
,,   2. Lower or grey chalk,    .    ,,
,,   3.       ,,      .    ,,
,,   4. Carboniferous limestone, .    Kilkenny, Ireland.
,,   5.       ,,      .    Charlestown, Scotland.
,,   6.       ,,      .    ,,
,,   7.       ,,      .    Lancashire, England.
,,   8.       ,,      .    ,,
,,   9. Cement rock, .    .    .    Lehigh Valley, Pennsylvania, U.S.A.

## Raw Cement Mixtures.

No. 1. From white chalk and Medway mud.
,,   2.   ,,   grey chalk and gault clay.
,,   3.   ,,   blue lias limestone and clay.
,,   4.   ,,   carboniferous limestone and clay.
,,   5.   ,,   calp limestone and shale, Dublin ; and limestone from Kildare.
,,   6.   ,,   hard crystalline limestone and white clay, New South Wales.
,,   7.   ,,   lower carboniferous limestone, limestone shale, and fresh-water river alluvium.

All these, except the first two, are dry process mixtures.

RESULTS OF ANALYSES OF RAW CEMENT MIXTURES.

| | No. 1. | No. 2. | No. 3. | No. 4. | No. 5. | No. 6. | No. 7. |
|---|---|---|---|---|---|---|---|
| *Insoluble siliceous matter, | 6·57 | 2·50 | 2·58 | 5·57 | 12·31 | 7·18 | 7·49 |
| Silica, | 7·63 | 11·83 | 11·41 | 9·61 | 2·74 | 8·49 | 7·15 |
| Alumina, | 4·32 | 5·23 | 4·80 | 3·45 | 3·06 | 3·90 | 3·69 |
| Oxide of iron, | 1·89 | 1·97 | 2·34 | 2·42 | 1·87 | 2·01 | 1·58 |
| Iron pyrites, | ·27 | | ·43 | ... | ·95 | ... | ‡ |
| Carbonate of lime, | 75·39 | 74·18 | 74·09 | 75·89 | 75·01 | 76·24 | 75·46 |
| Carbonate of magnesia, | 1·54 | 1·29 | 2·61 | 1·50 | 2·34 | 1·06 | 3·19 |
| Sulphate of lime, | ·17 | ·18 | ·21 | ·16 | +{ | ... | ·08 |
| Potash, | * | ·90 | ·93 | ·88 | +{ ++++ | ·84 | * |
| Soda, | * | ·31 | ·46 | ·39 | +{ | ·15 | * |
| Combined water, | 1·42 | 1·82 | ·43 | ·61 | ·71 | 1·79 | ·50 |
| | 99·20 | 100·21 | 100·29 | 100·48 | 98·99 | 100·66 | 99·14 |
| *Consisting of— | | | | | | | |
| Silica, | 5·83 | 2·27 | 2·27 | 5·03 | 10·77 | 6·57 | 6·56 |
| Alumina with trace of iron, | ·49 | ·23 | ·31 | ·54 | ·96 | ·56 | ·55 |
| Lime, | ·21 | ... | ... | ... | ·30 | ... | ... |
| | 6·53 | 2·50 | 2·58 | 5·57 | 12·03 | 7·13 | 7·11 |

* Not determined.    ‡ Trace.

**Analyses of Portland Cement and Rotary Kiln Clinker.**—The following analyses are those of Portland cements of known good quality, made from materials derived from widely different sources. The analyses of rotary kiln clinker were made upon clinker taken at the kilns from the coolers, consequently before the addition of gypsum added while grinding to regulate the setting time.

## Portland Cement.

No. 1. From white chalk and Medway mud.
„ 2.   „   grey chalk and gault clay.
„ 3.   „   blue lias limestone and clay.
„ 4. ‧ „   chalk marl and alluvial clay.
„ 5.   „   white chalk and boulder clay.
„ 6.   „   carboniferous limestone, shale, and alluvial clay.
„ 7.   „       „        „        „
„ 8.   „   carboniferous limestone and shale.

RESULTS OF ANALYSES OF VARIOUS SAMPLES OF PORTLAND CEMENT.

| | No. 1. | No. 2. | No. 3. | No. 4. | No. 5. | No. 6. | No. 7. | No. 8. |
|---|---|---|---|---|---|---|---|---|
| Insoluble siliceous matter, . . . | 2·89 | 1·23 | 4·55 | 1·65 | 1·35 | 1·49 | 1·22 | 1·40 |
| Silica, . . . | 21·30 | 21·33 | 16·86 | 21·79 | 20·92 | 20·12 | 20·70 | 19·74 |
| Alumina, . . . | 6·59 | 9·17 | 6·36 | 6·71 | 7·46 | 6·71 | 6·88 | 5·97 |
| Oxide of iron, . . | 5·38 | 4·16 | 4·83 | 4·62 | 4·97 | 4·03 | 4·04 | 4·73 |
| Lime, . . . | 61·45 | 61·06 | 62·50 | 61·38 | 59·63 | 60·99 | 63·67 | 62·88 |
| Magnesia, . . . | ·44 | 1·32 | 2·36 | 1·65 | 1·34 | 2·29 | 1·53 | 2·63 |
| Sulphate of lime, . | 1·42 | ·80 | 1·58 | ·80 | 1·86 | 1·89 | 1·24 | 1·54 |
| Water and carbonic acid, . . . | ... | ... | ... | ... | 2·06 | 1·70 | ... | ·74 |
| Potash, . . . | ·43 | ·73 | ·97 | ·89 | * | * | * | * |
| Soda, . . . | ·42 | ·40 | ·52 | ·53 | * | * | * | * |
| | 100·32 | 100·20 | 100·57 | 100·02 | 99·159 | 92·22 | 99·28 | 99·63 |

## Rotary Kiln Clinker.

No. 1. From Ransome's kiln,   .   .  1890. Dry process.  Fuel, producer gas.
„ 2.   „   Rudersdorf, nr. Berlin,  .  1903.   „    „      „   powdered coal.
„ 3.   „   Thames,   .   .   .  1902. Wet  „      „        „
„ 4.   „   Klagstrop, South Sweden,  1903.   „   „      „        „
„ 5.   „   Thames,   .   .   .  1902.   „   „      „   oil.
„ 6.   „   Sussex, .   .   .   .  1901.   „   „      „   powdered coal.
„ 7.   „   Medway,   .   .   .  1901.   „   „      „        „
„ 8.   „   Lehigh Valley, Pennsylvania,   .   .  } 1898. Dry  „      „        „
„ 9.   „   Thames,   .   .   .  1903. Wet  „      „        „
„ 10.   „   Medway,   .   .   .  1903.   „   „      „        „

\* Not determined.

ANALYSES OF VARIOUS SAMPLES OF ROTARY KILN CLINKER.

| | No. 1. | No. 2. | No. 3. | No. 4. | No. 5. | No. 6. | No. 7. | No. 8. | No. 9. | No. 10. |
|---|---|---|---|---|---|---|---|---|---|---|
| Insoluble residue, | 2·36 | ·25 | ·48 | ·19 | ·21 | ·29 | ·45 | ·35 | ·56 | ·49 |
| Silica, | 18·43 | 22·53 | 23·19 | 23·46 | 27·16 | 23·26 | 22·49 | 22·80 | 25·24 | 23·31 |
| Oxide of iron, | 4·45 | 5·95 | 5·41 | ·3·91 | 4·42 | 4·66 | 5·60 | 3·75 | 6·84 | 4·37 |
| Alumina, | 7·23 | 5·82 | 8·35 | 5·68 | 6·57 | 7·94 | 7·34 | 6·04 | 5·89 | 6·28 |
| Lime, | 65·44 | 60·33 | 59·87 | 61·74 | 58·33 | 61·54 | 59·66 | 61·78 | 58·99 | 60·99 |
| Sulphate of lime, | ·16 | 2·82 | ·92 | 1·16 | ·33 | ·35 | ·50 | 2·13 | ·71 | ·68 |
| Magnesia, | 1·91 | 2·07 | 1·09 | 1·70 | 1·17 | ·88 | 1·15 | ·92 | 1·37 | 1·08 |
| Potash, | ·07 | * | * | * | * | * | * | * | * | * |
| Soda, | ·11 | * | * | * | * | * | * | * | * | * |
| Loss on ignition, | ... | ... | ·25 | ·64 | 1·54 | ·46 | 1·56 | 1·37 | ·19 | 2·20 |
| | 100·16 | 99·77 | 99·56 | 98·48 | 99·73 | 99·38 | 98·75 | 99·14 | 99·79 | 99·40 |

* Not determined.

**Calculation of Proportion of Raw Materials.**—From the results of the analysis of the raw materials, the proportion in which they should be mixed may be calculated. Le Chatelier states that the proportion of lime in Portland cement of good quality should not be greater than that required by the formula :—

$$\frac{CaO + MgO}{SiO_2 + Al_2O_3} = 3,$$
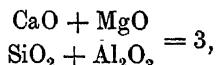
or less than that required by :—

$$\frac{CaO + MgO}{SiO_2 - Al_2O_3 - Fe_2O_3} = 3.$$
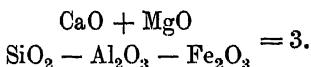
In both formulas the quantities indicated are equivalents, and not weights. These formulas assume that magnesia is equivalent to, and functions as, lime. This is disputed by Dr. Erdmenger,* who eliminates the magnesia, and writes the formula—

$$\frac{CaO}{SiO_2 + Al_2O_3} = 3,$$
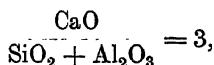
stating that it may give a product too high in lime, and that many cements of good quality are represented by—

$$\frac{CaO}{SiO_2 + Al_2O_3} = 2 \cdot 5.$$
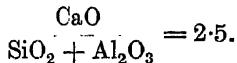
Highly siliceous clays require more lime than those rich in alumina, but by the preceding formulas the lime can only be proportioned to the silica and alumina taken together. Based upon the result of researches, which will be referred to in a later chapter, Messrs. Newberry represent the composition of Portland cement by the following formula, in which the magnesia is disregarded, and the lime is proportioned to the relative quantities of silica and alumina present :—

$$X (3CaOSiO_2) + Y (2CaOAl_2O_3).$$
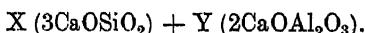
$3CaOSiO_2$ corresponds to $2 \cdot 8$ parts of lime by weight to 1 part of silica, and $2CaOAl_2O_3$ represents $1 \cdot 1$ part of lime to 1 of alumina. Substituting weights for equivalents, the formula reads :—

$$Lime = Silica \times 2 \cdot 8 + Alumina \times 1 \cdot 1.$$

To illustrate the method of calculating from this formula, we will take a

* *Chem. Zeit.*, 1893, vol. xvii., p. 982.

carboniferous limestone and a boulder clay of which the analyses are as follows :—

|  | Limestone. | Clay. |
|---|---|---|
| Silica, . . . . . . . . | 2·06 | 55·77 |
| Alumina, . . . . . . . | ·35 | 17·76 |
| Oxide of iron, . . . . . . . | 1·32 | 9·23 |
| Lime, . . . . ., . . . | 51·99 | 4·38 |
| Magnesia, . . . . . . . | ·66 | 2·93 |
| Loss on ignition, . . . . . . | 43·12 | 8·96 |
|  | 99·50 | 99·03 |

LIMESTONE.

| Per cent. silica, . . . . . . | 2·06 × 2·8 = 5·76 |
|---|---|
| ,, alumina, . . . . . . | ·35 × 1·1 = ·38 |
|  | 6·14 |

That is, 6·15 parts of lime are required for the silica and alumina present in limestone, leaving $51·99 - 6·15 = 45·84$ parts available for combination with the silica and alumina in clay.

CLAY.

| Per cent. silica, . . . . . . | 55·77 × 2·8 = 156·15 |
|---|---|
| ,, alumina, . . . . . . | 17·76 × 1·1 = 19·53 |
|  | 175·68 |
| Deduct lime contained in 100 parts clay, . . . . | 4·38 |
|  | 171·30 |

That is, 171·3 parts of lime are required for the silica and alumina contained in the clay. In the limestone 45·84 per cent. of lime is available ; therefore, for 100 parts of clay there are required $\dfrac{171·3 \times 100}{45·84} = 373·6$ parts of limestone. The percentage of carbonate of lime in this mixture is calculated as follows :—

100 parts of clay contain 4·38 × 1·7843 = 7·81 parts of carbonate of lime.
100 parts of limestone contain 51·99 × 1·7843 = 92·76 parts of carbonate of lime.

373·6 parts of limestone will contain $\dfrac{92·76 \times 373·6}{100} = \left\{ \begin{array}{l} 346·5 \text{ parts of carbonate} \\ \text{of lime.} \end{array} \right.$

The mixture thus consists of :—

| 100 | parts of clay containing | 7·81 parts of carbonate of lime. |
|---|---|---|
| 373·6 | ,, limestone containing | 346·50 ,, ,, |
| 473·6 | ,, mixture containing | 354·31 ,, ,, |

Carbonate of lime per cent. $\dfrac{354·31 \times 100}{473·6} = 74·81.$

The proportions of the raw materials are frequently calculated so as to give a desired percentage of carbonate of lime in the mixture. Whatever may be the composition of the materials, if they are suitable for the manufacture of Portland cement, this percentage will vary between very narrow limits, and will lie between 75 to 77 or 77·5 per cent. In most cases from 75 to 76 per cent. will give the best results, except perhaps when using very siliceous clays, when the carbonate of lime may reach to 77·5 or even 78 per cent. The relative proportions of the two materials may be determined by the following simple rules :—

1. From the percentage of carbonate of lime contained in the chalk or limestone deduct the percentage required in the mixture, the result will be the weight of clay or shale needed.

2. From the required percentage of carbonate of lime in the mixture deduct the percentage contained in the clay or shale, the result will be the weight of limestone to be used.

For example, let us assume the case of a clay or shale containing 25 per cent. of carbonate of lime and a chalk or limestone containing 91 per cent., both materials being in the dry condition, 76 per cent. of carbonate of lime being required in the mixture. The relative proportions then are :—

$$91 - 76 = 15 \text{ parts clay or shale.}$$
$$76 - 25 = 51 \text{ parts chalk or limestone.}$$
$$15 \text{ parts of clay or shale contain } \frac{25 \times 15}{100} = 3\text{·}75 \text{ parts of carbonate of lime.}$$
$$51 \text{ parts of chalk or limestone contain} \frac{91 \times 51}{100} = 46\text{·}41 \qquad \text{,,} \qquad \text{,,}$$
$$51 + 15 = 66 \text{ parts of mixture contain } 46\text{·}41 + 3\text{·}75 = 50\text{·}16 \qquad \text{,,} \qquad \text{,,}$$
$$\text{Carbonate of lime in mixture } \frac{50\text{·}16 \times 100}{66} = 76 \text{ per cent.}$$

Obviously, by multiplying each of these proportionate quantities by the same number any convenient weights of the materials may be employed. If the manufacture is by the wet process, allowance must be made for the water present in the materials. In the example given we will assume that these proportions are as follows :— Clay containing 22, and chalk containing 16 per cent. of water in the condition in which they are weighed into the wash-mill. 100 parts of clay then contain 78, and 100 of chalk 84 parts of solid matter.

The relative proportions then are—

$$\text{Clay} \frac{100 \times 15}{78} = 19\text{·}23.$$

$$\text{Chalk} \frac{100 \times 51}{84} = 60\text{·}71.$$

This calculation assumes that magnesia is present in such small quantity that it may be disregarded, lime being considered to be the only base present. Magnesia combines with the silica and alumina of the clay, as lime does, and it may occur in certain materials in sufficient quantity to be considered as a base, while at the same time cement made from such materials may be quite normal, and as regards magnesia fall within specification requirements. In cases of this kind, the lime must be proportionately reduced, magnesia being considered as equivalent to lime, with due regard to the difference in their molecular weights. The molecular weight of carbonate of lime is 100, that of carbonate of magnesia 84·36, therefore 1·185 parts of carbonate of magnesia are equivalent to 1 of carbonate of lime. For example, assuming that the limestone considered in the previous calculation contained 1·5 per cent. of carbonate of magnesia, chalk is not likely to contain as much, many limestones do ; and the shale or clay 2·5 per cent., the calculation would now be as follows :—

The carbonate of lime equivalent of the carbonate of magnesia in the limestone is $1·5 \times 1·185 = 1·777$. This added to the actual carbonate of lime gives 92·777 per cent. of bases.

The carbonate of lime equivalent of the carbonate of magnesia in the clay or shale is $2·5 \times 1·185 = 2·962$. This added to the actual carbonate of lime gives 27·962 per cent. of bases. If 76 per cent. of bases are required in the mixture the calculation is now as follows, the previous rules applying :—

$$92·777 - 76 = 16·777 \text{ parts of clay or shale.}$$

$$76·000 - 27·962 = 48·038 \text{ parts of limestone.}$$

$$16·777 \text{ parts of clay or shale contain } \frac{27·962 \times 16·777}{100} = 4·691 \text{ parts of bases.}$$

$$48·038 \text{ parts of limestone contain } \frac{92·777 \times 48·038}{100} = 44·568 \text{ parts of bases.}$$

$$16·777 + 48·038 = 64·815 \text{ parts of mixture contain}$$

$$44·568 + 4·691 = 49·259 \text{ parts of bases.}$$

$$\text{Bases in mixture } \frac{49·259 \times 100}{64·815} = 76·01 \text{ per cent.}$$

The correction for water is made if required as in the previous example.

The composition of the finished cement cannot be accurately calculated from that of the raw mixture, as the results are influenced by the ash of the fuel. For this reason, the results obtained from samples burned in trial kilns with solid fuel cannot successfully be compared with those obtained from the same mixture of materials burned on the manufacturing scale, as in the trial kiln the quantity of fuel needed amounts to from twice to three times that necessary in large kilns. This is equally true if samples are burned by gaseous fuel—we have seen perfect clinker obtained in the laboratory from a small rotary kiln fired by town gas—as these results are obviously

not comparable with those obtained in manufacture by the use of solid
fuel. Our own practice, when samples are required, is to burn a fairly large
one, say of 3 or 4 cwts. or even more, in a kiln of sufficient size, sifting the
product through a sieve of about ⅛ inch mesh, rejecting about half the
dust and grinding the remainder with the bulk of the sample. The results
of chemical analysis will, to those familiar with the subject, generally indicate
whether the proposed raw materials are suitable or not, but samples are
often asked for and are, indeed, sometimes necessary.

**Rapid Methods of Testing the Accuracy of Cement Raw Mixtures.**— The
accuracy of the raw mixture requires to be continually tested, and it is
essential that the tests should be rapidly made, so that the proportions,
if inaccurate, may be readjusted without delay. Many methods are in use
for making these tests, but it is necessary that the results from the one em-
ployed should, in the first place, be verified by comparison with those obtained
from a normal sample of the raw mixture in use, the composition of which
has been accurately determined. A simple method, but one which involves
at least two weighings and is somewhat tedious, is by determining the loss
on ignition of about ·5 gramme of the sample previously dried at 100°. It
is ignited at about 1,000° in a platinum crucible in a muffle, or more con-
veniently in an electric furnace to constant weight. Although quite accurate
when compared with the result obtained from a normal sample, it is now
rarely employed, as it is more rapid and convenient to obtain the result
required alkalimetrically, or by a gas volumetric method.

**Testing Raw Mixtures by Alkalimetry.**—To a weighed quantity of the
sample an excess of deci-normal hydrochloric acid is added in known volume
in an Erlenmeyer flask, the excess being titrated back with sodium hydrate
solution, using methyl-orange as an indicator. The details of the process,
and the preparation of the standard solutions, are too well known to need
repeating here. A method of determining both lime and magnesia has been
described by Spencer B. Newberry,* who worked it out in the laboratory
of the Sandusky Portland Cement Company. It deserves special notice,
and is based on the facts that magnesium hydrate is sufficiently soluble
in water to colour phenol-phthalein, and that magnesia is completely pre-
cipitated and separated from lime by caustic soda, in dilute solution on
boiling. We give the author's description of the process :—

" Prepare one-fifth normal hydrochloric acid and one-fifth normal caustic
soda solutions, and standardise with pure transparent Iceland spar. One-
half gramme of spar should exactly neutralise 50 c.c. of acid.

" Weigh out one-half gramme of finely ground limestone, transfer to
an Erlenmeyer flask of about 500 c.c. capacity provided with rubber stopper
and thin glass tube about 30 inches long to serve as a condenser. Run into
the flask 60 c.c. one-fifth normal acid, attach the condenser, and boil gently

*Cement and Engineering News.   Chicago.   Vol. xiv., 1903, p. 35.

for about two minutes, allowing no steam to escape from the tubes. Wash down the tube into the flask with a few c.c. of water from a wash bottle, remove the condenser, and cool the solution thoroughly by immersing the bottom of the flask in cold water. When quite cold, add five to six drops of phenol-phthalein solution (1 gramme in 200 c.c. alcohol) and titrate back to first pink colour with one-fifth normal soda solution. It is important to recognise the point at which a faint pink colour first appears throughout the solution, even though this may fade out in a few seconds. If alkali be added to a permanent and strong red colour, the lime will come too low. Let us call the amount of acid used the first acid, and the alkali used to titrate back, the first alkali.

" In case of materials containing only insignificant proportions of magnesia, the operation ends here, and the calculation is simply—No. of c.c. acid — No. of c.c. alkali × 2 × 0·56 = per cent. CaO. In this case, it is unnecessary to cool the solution, and a permanent red is obtained at the point of neutralisation. To determine magnesia, we proceed as follows :—

" Transfer the neutral solution to a large test-tube 12 inches long and 1 inch inside diameter, marked with a paper strip or otherwise at 100 c.c. Heat to boiling, and add one-fifth normal soda solution about 1 c.c. at a time, boiling for a moment after each addition till a deep red colour, which does not become paler on boiling, is obtained. This point can be easily recognised within one-half c.c. after a little practice. Note the number of c.c. soda solution added to the neutral solution as second alkali. Dilute to 100 c.c.,* boil for a moment, and set the tube aside to allow the precipitate to settle. When settled, take out 50 c.c. of the clear solution, by means of a pipette, and titrate back to colourless with one-fifth normal acid. Multiply by 2 the number of c.c. acid required to neutralise, and note as second acid.

" The calculation is as follows :—

" Second alkali — second acid × 2 × 0·40 = per cent. of MgO.

" First acid — (first alkali + second alkali — second acid) × 2 × 0·56 = per cent. CaO.

" *Example.*— To one-half gramme limestone were added 60 c.c. acid (first acid). To titrate back to first pink, 11·60 c.c. alkali were required (first alkali). The solution was then transferred to test-tube, boiled, and 3·55 alkali added to permanent deep red colour (second alkali). After diluting to 100 c.c. and settling, 50 c.c. of the red solution required 0·45 c.c. acid to decolourise it (0·45 × 2 = 0·90 = second acid).

" (3·55 — 0·90) × 2 × 0·40 = 2·12 per cent. of MgO.

" 60·00 — (11·60 + 3·55 — 0·90) × 2 × 0·56 = 51·24 per cent. of CaO.

* We have found it difficult, when removed from flask to test-tube, to keep the solution to as small a volume as 100 c.c., and prefer to transfer it to a 200 c.c. flask, taking out 100 c.c.

" If results are desired in percentages of magnesium carbonate and calcium carbonate, the factors 0·84 and 1·00 are to be substituted for 0·40 and 0·56 respectively.

" Not more than 1 c.c. excess of alkali should be added in precipitating the magnesia, the second acid should, therefore, not exceed 1·0. Larger excess of alkali tends to throw down lime. The settling usually requires only a few minutes, unless much magnesia is present; it may be greatly hastened by allowing the test-tube to stand two or three minutes, and then immersing the lower part for a moment in cold water.

" The tendency of the method is to give slightly too high results on magnesia, and too low results on lime. This is partly due to the formation of calcium carbonate by the action of the carbon dioxide of the air during the precipitation of the magnesia. By the use of a large test-tube, as before described, this error is so far reduced as to be insignificant. Filtration of the solution was found impracticable, owing to the formation of carbonate. Much soluble alumina and iron oxide obscure to some extent the end reaction in the first and second titration. Alumina is, however, precipitated by soda, with the formation of no pink colour, until the precipitation is complete. The soluble alumina present is not, therefore, added to the magnesia in the result obtained.

" Analysed, as above described, a mixture containing 90 per cent. $CaCO_3$ (Iceland spar) and 8 per cent. $MgCO_3$ gave $CaCO_3$ 89·8, $MgCO_3$ 8·32. Limestones analysed volumetrically as above, also by precipitation of lime as oxalate and titration with permanganate and determination of magnesia as pyrophosphate, gave the following results. The gravimetric determinations of magnesia were made by single precipitation, except in No. 2, in which case the precipitate of calcium oxalate was dissolved and re-precipitated."

| No. | Volumetric | | Permanganate and Gravimetric. | |
|---|---|---|---|---|
| | CaO. | MgO. | CaO. | MgO. |
| 1, . . . | 36·62 | 12·48 | 36·97 | 12·60 |
| 2, . . . | 47·82 | 5·72 | 47·70 | 5·73 |
| 3, . . . | 51·24 | 2·12 | 51·28 | 2·02 |
| 4, . . . | 29·62 | 20·04 | 29·92 | 20·03 |

In this country, the separate determination of magnesia is not generally necessary, as, in the raw materials usually employed, it occurs in quantity so small that its presence may be disregarded, but there are exceptions in which care has to be taken that it is not present in excess. In America its occurrence in sufficient quantity to require great care in the selection

of raw materials is not unusual. Most American specifications allow a quantity of magnesia not exceeding 4 per cent. in Portland cement.

**Gas Volumetric Methods, Calcimeters.**—A method very generally employed for rapidly estimating the amount of calcium carbonate in cement raw materials and mixtures is by measuring the volume of carbon dioxide evolved by treating a weighed quantity of the material with hydrochloric acid, and from this volume calculating the amount of calcium carbonate present. Many special forms of apparatus known as calcimeters have been devised for this purpose, with tables for facilitating, or dispensing with, calculations. The results from any of them are only approximately accurate, but they are sufficiently so for technical purposes. A portion of the carbon dioxide evolved is retained by the acid used for the decomposition, and the quantity varies with the volume given off, and with the temperature, and pressure prevailing at the time the determination is made. We describe the instruments most generally used.

**Scheibler's Calcimeter.**—An instrument, devised by Dr. Scheibler, for determining the amount of calcium carbonate present in the animal charcoal used for sugar refining, has been frequently employed for making a similar determination in Portland cement mixtures. A description of the apparatus, with instructions for its use, will be found in several text-books of analytical chemistry,* and they need not be repeated here. The principle of its action is this :—The carbon dioxide evolved by the action of hydrochloric acid upon a weighed quantity of the material to be tested displaces a corresponding volume of water from a graduated tube. To the volume, when read off, is added a correction to allow for the carbon dioxide retained by the acid used for the decomposition. Scheibler gives 0·8 c.c. as the volume to be added to that read off. Warrington † points out that this is not a constant quantity, but is dependent upon the volume evolved, and fixes 7 per cent. of this volume as the quantity to be added. The total volume is reduced to standard conditions, and from this the calcium carbonate is calculated. It has been suggested that, with this apparatus, corrections may be dispensed with by making a determination with pure calcium carbonate—the relation between this amount and that contained in an equal weight of the material tested being a simple proportion statement. For testing cement mixtures, it would be better to use as a standard a sample of the same material of which the composition is known. The result of any determination with the standard, of course, only holds good for comparison so long as both temperature and pressure remain unchanged. A second instrument may be employed, and the confined volume may be adjusted as the temperature and pressure alter, but for working in com-

* Fresenius, *Chemical Analysis—Quantitative*, vol. i., p. 344, 7th ed. ; Sutton's *Volumetric Analysis*, p. 87, 5th ed. ; Crooke's *Select Methods in Chemical Analysis*, p. 567, 3rd ed.                                      † *Chemical News*, vol. xxxi., p. 253.

parison with a standard, Dr. Lunge's nitrometer, the use of which will be presently described, is a much more delicate and convenient instrument.

**Dietrich's Calcimeter.**—A more modern appliance, and, at the same time, one of the best forms of calcimeter, is that of Dietrich. The measuring tube is graduated into 100 c.c., each of which is sub-divided into fifths. This is connected with the levelling tube by thick-walled rubber tubing, the connections being securely bound with wire. Either water or mercury may be used as the confining liquid; the latter is preferable. The tubes are held by clamps attached to a vertical rod which is secured to a cast-iron base plate. An ordinary retort stand answers this purpose sufficiently well. The top of the measuring tube is drawn out to a smaller tube, closed by a short piece of rubber tubing and a pinch cock, a short branch tube is connected with the drawn-out portion, but fixed at right angles to it. The gas generating bottle is of about 150 c.c. capacity, with a wide mouth closed by a rubber stopper, through the centre of which passes a short piece of glass tube. This tube reaches just through the stopper, and is raised sufficiently above it to admit of connection with a rubber tube, which connects the bottle with a coil made of copper or brass pipe of small diameter. This coil is of such a diameter that the generating bottle will easily enter it, and it stands in a tin or copper cylinder containing water. The other end of the coil is connected with the branch on the side of the measuring tube by a sufficient length of rubber tubing, the cylinder with coil and the generating bottle standing on the working bench. The tube for containing the acid is made of gutta percha or vulcanite, and is of such dimensions as to contain 5 c.c. of acid without danger of spilling, when leaning at an angle of about 45° in the generating bottle. Either a good aneroid or a Bunsen barometer is necessary, and two thermometers—one for the air, the other for the cylinder containing the coil, the water in which must be maintained at the same temperature as the air. This instrument gives a constant volume for any one sample of material tested, whatever the temperature and pressure; the weight to be taken for the determination consequently varies with the readings of the thermometer and barometer. A table supplied with the apparatus gives the weight for all ordinary temperatures and pressures, and a second table gives the requisite correction for the absorption by the 5 c.c. of hydrochloric acid employed for the decomposition. The weights are so arranged that the indicated volume as read off, plus the number for that volume from the absorption table, gives the percentage of carbonate of lime without further calculation.

Before commencing a determination the height of the barometer and the temperature are noted. These are referred to in the table, and the corresponding weight is ascertained. The required quantity of the dry material is accurately weighed and transferred to the generating bottle. The tube containing 5 c.c. of hydrochloric acid is carefully inserted into the bottle,

and is allowed to lean against the side. Commercial hydrochloric acid answers the purpose very well, and is most conveniently measured from a burette, which may be automatically filled from a stock bottle. The pinch cock at the top of the measuring tube is next opened, the stopper is inserted into the bottle, and the level of the confining liquid is carefully adjusted to the zero mark. The pinch cock is then closed, the whole of the liquid is brought into contact with the weighed carbonate, by inclining the bottle, using the right hand, the levelling tube being at the same time lowered with the left hand. The bottle is well shaken, placed in the cylinder of water containing the coil, and the levels are roughly adjusted. The bottle will be heated by the hand of the operator, and some heat is also generated by the action of the hydrochloric acid on the carbonate. By the use of the condenser both the bottle and the evolved gas are brought to the temperature of the air. The bottle is from time to time taken from the cylinder, well shaken, and replaced. This is important, as with some materials the liquid retains the carbon dioxide with great obstinacy. Causes contributing to this are the presence of bituminous matter, magnesium carbonate, and silica in the gelatinous state.

When the evolution is complete the bottle is allowed to remain in the condenser, and the tubes are levelled. The volume is read off, and the correction for absorption is added. The resulting number gives the percentage of carbonate of lime in the sample tested.

**Faija's Calcimeter.**—The Faija calcimeter is a modified form of the Dietrich apparatus. A pamphlet containing the tables and likewise a full description of the method of using it is supplied with the instrument, but a brief description may be given here. A constant weight of the materials to be tested is taken, the gas volume for any one sample consequently varies with the temperature and pressure. The temperature only need be taken into consideration, as the volume is always measured under the standard pressure of 760 mm. In the arrangement for effecting this, and in the graduation of the measuring tube, the instrument differs from that of Dietrich. The variation in construction is as follows :—The upper end of the levelling tube is drawn out in a similar manner to the lower one, and to this a flexible tube is fastened, which is connected with an aneroid barometer secured to a board which forms the back of the instrument, and to which the tubes are attached. The flexible tube is sufficiently long to admit of the raising and lowering of the levelling tube. A short flexible tube with an india-rubber ball at the end is also connected with the barometer. By a simple piece of mechanism, the barometer may be brought to standard conditions according as the ball is flattened to a greater or less extent between a disc and the board forming the back of instrument. Above the barometer a tap is placed. When this tap is open, the levelling tube is in communication with the outer air ; when it is closed it communicates with the baro-

meter.  A second tap at the upper end of the measuring tube allows the communication between this and the tube from the generating bottle to be closed.  The flexible tube and pinch cock at the top of measuring tube in the Dietrich apparatus is in this type of instrument replaced by a tap.  The confining liquid is water.  The method of making a determination is the same in both cases, except as regards the final measurement of the gas volume.  The weight of material taken is 0·65 gramme, the quantity of hydrochloric acid 10 c.c., and the carbon dioxide is evolved and the tube approximately levelled at the atmospheric pressure.  The taps of the measuring tube and above the barometer are then closed, and the barometer is adjusted by compressing or expanding the india-rubber ball until it indicates the standard pressure of 760 mm.  The tubes are then accurately levelled, the volume is read off, and the temperature is noted.  These numbers are referred to a table which is so arranged that the percentage of carbonate of lime may be at once read off.  No correction for absorption is necessary, as this is allowed for in graduating the measuring tube.

**Lunge's Nitrometer.**—This apparatus may be used for testing raw materials or mixtures.  The most suitable form is that with the cup or funnel on the top of the measuring tube, and fitted with the Greiner-Freidrich tap, mercury being used as the confining liquid.  The nitrometer, from its wide applicability, is so well known to all chemists that it need not be described here.  To adapt it for the determination of carbon dioxide, a wide-mouthed Erlenmeyer flask, of about 150 c.c. capacity, is fitted with a well-fitting rubber stopper, through which a short piece of glass tube passes.  By means of this it is connected with the bent tube from the tap by about 3 inches of strong rubber tubing.  The acid is contained in a glass or ebonite tube which leans against the side of the flask, and contains 5 c.c. when half-filled.  Dr. Lunge uses the nitrometer for the determination of carbon dioxide, taking 5 c.c. of acid for the decomposition, and calculating the quantity to be added for absorption from the following table by Dietrich :—

TABLE SHOWING THE ABSORPTION OF CARBON DIOXIDE BY 5 C.C. HYDROCHLORIC ACID OF SPECIFIC GRAVITY 1·125.

| Given off, c.c., . | 1 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 |
| Absorbed, c.c., . | 1·85 | 2·00 | 2·31 | 2·62 | 2·93 | 3·24 | 3·55 | 3·86 | 4·17 |
| Given off, c.c., . | 18 | 20 | 22 | 24 | 26 | 28 | 30 | 32 | 34 |
| Absorbed, c.c., . | 4·48 | 4·79 | 4·96 | 4·98 | 5·03 | 5·06 | 5·09 | 5·11 | 5·14 |
| Given off, c.c., . | 36 | 38 | 40 | 42 | 44 | 46 | 48 | 50 | 55 |
| Absorbed, c.c., . | 5·17 | 5·20 | 5·23 | 5·25 | 5·27 | 5·30 | 5·32 | 5·35 | 5·41 |
| Given off, c.c., . | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
| Absorbed, c.c., . | 5·48 | 5·55 | 5·62 | 5·69 | 5·76 | 5·83 | 5·90 | 5·97 | 6·04 |

The figures found in the second line should be added to those read off in the first line, *before* reducing the volume to 0° and 760 millimetres.

For testing cement mixtures we prefer to work in comparison with a normal sample of the same material, of which the composition is accurately known, and which is used as a standard. Two similar nitrometers of 50 c.c. capacity subdivided into $\frac{1}{10}$ c.c. are employed, and they must agree absolutely with each other. We believe these instruments can now be obtained with the National Physical Laboratory certificate of accuracy. The quantity of material taken is ·2 gramme, and of hydrochloric acid 2 c.c. The acid is conveniently delivered from a burette with automatic supply. Neither temperature, pressure, nor absorption need be regarded. To make a determination the taps are turned so that the measuring tube of each instrument communicates with the cup, and the mercury level is adjusted to the zero of the
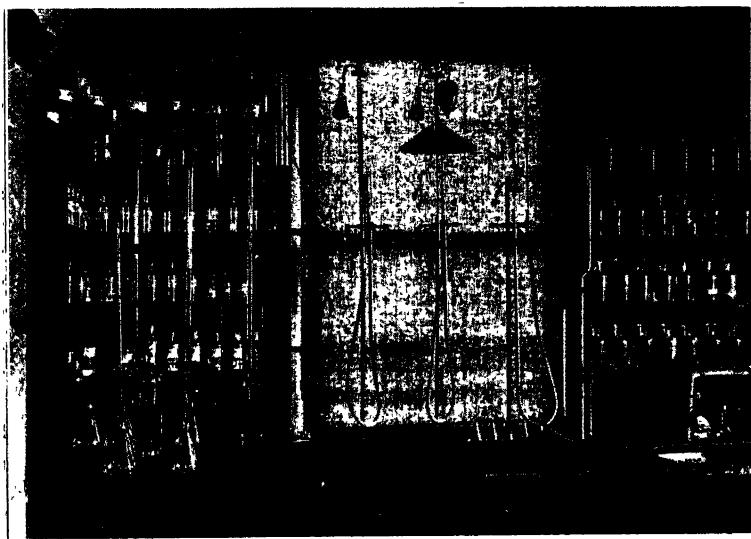
Fig. 3.—View in Laboratory, showing Apparatus for Rapid Control Tests.

scale. The weighed quantities of the material to be tested, and of the standard, are transferred to the respective flasks, the tubes with acid are inserted, and the flasks are then secured to the stoppers, which always remain attached to the instruments. Care should be taken to heat them as little as possible by handling. The taps are loosened, and after two or three minutes they are replaced and turned, so that the flasks are in communication with the measuring tubes. The acid is then brought into contact with the samples by tilting the flasks, the levelling tubes are lowered, and the levels roughly adjusted. The flasks are shaken occasionally until all the gas is evolved. As soon as the volumes remain constant they are read off, after the final

adjustment of the levels. If the volumes on both instruments agree the percentage of carbonates in the sample tested is equal to that in the standard, if they do not, a simple calculation gives the required result. With the volume of gas obtained from a normal cement mixture, if the variation falls within $\frac{1}{2}$ c.c. above or below the standard, $\frac{1}{10}$ c.c. may be taken as equivalent to ·2 per cent. of carbonate and a calculation avoided. The Erlenmeyer flasks used for these determinations should be of about 100 c.c. capacity.

Two aluminium capsules that exactly balance each other will be found very convenient for weighing the samples. This can be very quickly done on a short beam balance, which should be sensitive to $\frac{1}{10}$ milligramme. If only an occasional test is required a weighing may be saved by placing on one capsule a little of the standard material equal to about ·2 gramme, and using it as a weight for the sample to be tested, which is balanced on the other capsule.

An arrangement of appliances for rapid control tests is shown by Fig. 3. The nitrometers will be observed in the centre of the illustration.

**The Barker Carbonate Apparatus.**—This was designed by an American chemist, J. F. Barker, of the Ohio State University, for rapidly determining the carbonate of lime value of limestones before grinding them for agricultural purposes, and for enabling the purchaser to test the ground product for carbonate of lime. It is applicable to any carbonate, and it is claimed that the results obtained by unskilled users of this method, working without previous experience, compare favourably with the work of a skilled chemist using complicated apparatus. It is illustrated by Fig. 4, and is described by its inventor as follows :—

"The apparatus is based upon the principle of a hydrometer which takes account of the law that, when an object (the hydrometer) is immersed in a liquid, it is buoyed up by a force equal to the weight of the liquid displaced by the object. In this apparatus the carbon dioxide gas released by the sample decreases the weight. The apparatus consequently rises in the water in which it is immersed, recording on the graduated scale the percentage of carbonates from which the gas escaped.

"To analyse a sample of limestone for carbonates, measure out 40 c.c. hydrochloric acid (sp. gr. 1·15), pour this into the acid reservoir through the opening at A. With graduated stem disconnected, hang 10-gramme weight at B (this weight consists of a stem with flat top which is lowered into the tube). The hydrometer should then float in a cylinder of water, and be
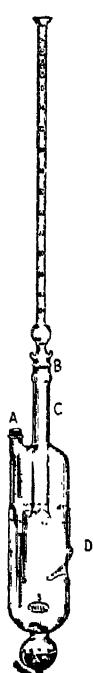


Fig. 4. — Barker's Carbonate Apparatus.

immersed to some point at C. The right amount of acid to be used is the amount that will cause the hydrometer with 10-gramme weight to sink somewhere along the graduated space at C. This should be approximately 40 c.c. Remove 10-gramme weight, and introduce pulverised limestone until instrument is immersed to exactly the same point. Now connect graduated stem and add water, a drop at a time, through the funnel-shaped top until immersed to zero point. Raise hydrometer out of water, and open stopcock D until acid drops slowly into reaction chamber, decomposing the limestone, then release so apparatus floats freely. Place a few drops of oil in the reaction chamber to minimise effervescence. Some limestones and other materials will froth badly and, in such cases, the acid must drop very slowly. As the reaction proceeds the instrument slowly rises, and at the conclusion, the point on stem at surface of water gives the percentage of calcium carbonate equivalent to the carbon dioxide in the sample. A Fahrenheit thermometer is hung inside the floating cylinder (hydrometer jar). Its reading is taken before and after each determination, to allow for any error due to change in temperature. To the figure for calcium carbonate equivalent add 0·5 for each degree rise, or subtract 0·5 for each degree fall in temperature between the two readings. This temperature change need seldom amount to more than a fraction of a degree."

The makers * of this instrument say :—" To be of value, this apparatus must be very accurate. Every hydrometer is thoroughly tested before leaving our works, and is accompanied by a certificate bearing the serial number of the apparatus and signed by the inventor."

The accuracy and practicability of the method are illustrated by the following results of analyses of limestone.† The figures for this method were obtained by a farm boy, without chemical training, or special aptitude for such work. They do not simply represent his best work, but are all the determinations he had made up to date. The other column gives results on the same samples obtained by a chemist using a standard laboratory method.

| Limestone No. | Calcium Carbonate Equivalent. | | Limestone No. | Calcium Carbonate Equivalent. | |
|---|---|---|---|---|---|
| | Hydrometer Method | Standard Method. | | Hydrometer Method. | Standard Method. |
| 200 | 80·0 | 80·0 | 230 | 83·5 | 83·2 |
| 201 | 81·5 | 81·7 | 240 | 99·5 | 99·0 |
| 220 | 78·5 | 78·6 | 244 | 98·5 | 98·5 |
| 221 | 71·0 | 71·1 | 254 | 97·5 | 97·7 |
| 223 | 78·5 | 78·7 | 256 | 89·0 | 88·9 |
| 224 | 83·0 | 84·0 | 257 | 95·5 | 95·8 |
| 226 | 82·5 | 82·9 | Calcite | 99·5 | 99·8 |

* The Will Corporation, 845 Maple Street, Rochester, N.Y.
† *Technical Bulletin*, No. 62, New York Agricultural Experiment Station, Geneva, N.Y.

**Specific Gravity.**—This test should be conducted in the chemical labora-tory, as the results obtained by an unskilled operator, even with suitable apparatus, may be very wide of the mark. The determination may be made with the ordinary specific gravity bottle, a liquid without action on cement being substituted for water. Either paraffin or turpentine is generally employed ; whichever liquid is used it must be absolutely free from water. This may be ensured by shaking it up with finely-ground fresh Portland cement, or by allowing it to stand over freshly-burnt quicklime. If the specific gravity bottle is employed, the specific gravity of the liquid must also be known. This should be determined with a specific gravity bottle, and not with a hydrometer, as is sometimes suggested. If a stock of liquid is kept, it should occasionally be re-determined, especially in the case of turpentine. This method leaves nothing to be desired as regards accuracy, but it is not generally employed, as several forms of apparatus have been devised in which the volume of liquid displaced by a known weight of cement is directly read off, and the specific gravity is calculated by dividing the weight of cement taken by the volume of liquid displaced, the specific gravity of which latter need not be known. Illustrations of several forms of instruments will be found in most catalogues of chemical apparatus ; some of those most generally used may be briefly described.

**Mann's Gravimeter.**—This, probably the first piece of apparatus of the kind, was fully described by its inventor in *Proceedings Inst. C.E.*, vol. xlvii., p. 251. It consists of a flask holding, when filled to a mark on the neck, 1,000 grains of water, and a burette with a stopcock containing an equal volume, less the quantity displaced by 1,000 grains of the heaviest substance intended to be examined. 1,000 grains of cement are weighed off and trans-ferred to the clean dry flask, or the flask may be counterpoised and the cement weighed in it. The burette is filled to the containing mark with whatever liquid is used, which is allowed to run into the flask until it is nearly filled to the mark. To expel the occluded air, some operators cork and shake the flask, which is a slovenly method. We prefer to hold it by the neck with a test-tube holder, and stir the contents with a stout knitting needle until no more air escapes. The adhering cement is washed off the needle by drawing it up through the liquid, which rapidly rises to the upper part of flask when the contents are allowed to remain at rest. More liquid is then allowed to run from the burette until the mark is reached. The stem of the burette is so graduated that the specific gravity is at once read off.

**Schumann's Volumemeter.**—This consists of a flask or bottle of about 150 c.c. capacity, into the neck of which is ground a tube graduated upwards from a short distance above the neck from 0 to 40 c.c., divided into tenths. The bottle and part of tube is filled to either 0 or one of the lower graduations with paraffin or turpentine, and 50 grammes of cement are allowed to fall down the tube into the liquid. The apparatus is carefully shaken to expel

the air, and the height of the liquid is read off on the tube. The difference of the readings gives the volume of liquid displaced. The chief trouble with this apparatus is caused by the cement, which, from having to follow the liquid down the tube, adheres to its sides. This may, however, be obviated by pouring the liquid down a funnel with a long narrow stem, which ought really to be supplied with the instrument. The cement can conveniently be introduced through an ordinary funnel with a short stem.

**Blount's Volumemeter.**—This is a simple piece of apparatus which is capable of giving good results. It consists of a flask with a broad flat bottom, containing exactly 64 c.c. when filled to a mark at the lower part of a slender neck, which is closed by a stopper. Above this mark the neck is divided into tenths. The first graduation is marked 14, and not 64; the neck, therefore, reads upwards from 14 to 17 c.c. To make a determination, 50 c.c. of liquid, either paraffin or turpentine, are delivered into the flask by a pipette; the neck is thus kept dry. 50 grammes of cement are then introduced, and the flask is shaken gently to expel the air. 14 c.c. of the displacement are accounted for by the flask to the first graduation, the remainder is read off on the stem. The volume of liquid displaced by 50 grammes of any sample of Portland cement will fall between 14 and 17 c.c.

**Keates' Double Bulb Specific Gravity Bottle.**—In this instrument a constant volume of liquid is employed, and a variable weight of cement. In those previously described the weight of cement has been constant, the volume of liquid varying. It consists of two bulbs placed one above the other, with a short neck between them, the lower bulb somewhat exceeding the upper one in capacity. The upper bulb has a short neck closed by a stopper. On the neck between the bulbs is a mark $b$, on the neck of the upper one is a similar mark $a$. The capacity of the upper bulb must be accurately determined, and may conveniently be 1,000 grains of water at 15·5° C. To make a determination, the lower bulb is filled with a pipette to the mark $b$ on the neck with whatever liquid is employed, and the flask is weighed. The cement is dropped carefully into the bottle through a funnel with a short stem until the liquid reaches the mark $a$, when the flask is again weighed. The weight of cement required to raise the liquid from $b$ to $a$ is its specific gravity.

**The Le Chatelier-Candlot Volumemeter.**—This is represented by Fig. 5. The lower part of the flask to the mark below the bulb contains about 100 c.c., the bulb from this line to the commencement of the graduations above exactly 20 c.c. The graduated portion of the neck contains 3 c.c. divided into tenths, reading upwards from 0 to 3. Sufficient of the water-free liquid used for the determination to fill the flask to the lower mark is introduced by means of a pipette. The determination may be made by two methods, 64 grammes of cement accurately weighed being required in each case.

1. *With a Varying Quantity of Cement.*—By means of a funnel, cement is carefully introduced into the flask until the liquid rises a few tenths of a c.c. above the zero mark on the neck, the flask being gently rapped on a soft pad to expel air as the operation proceeds. The remaining cement is weighed ; the difference between this weight and that of the original quantity is the weight that has displaced a volume of liquid equal to that of the bulb, plus that read off on the graduated stem.
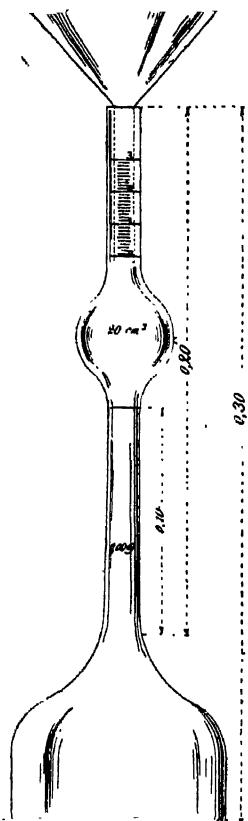


Fig. 5.—Le Chatelier Volumemeter.

2. *With the Whole Quantity of Cement.*— This is effected in exactly the same manner as in 1, the whole quantity of cement being introduced. The liquid now rises to some mark on the neck, its position depending on the higher or lower specific gravity of the cement. The volume is read off as below.

In each case the specific gravity is obtained by dividing the weight of cement by the volume of liquid displaced. When introducing the liquid, care should be taken to avoid contact with the portion of the stem above the bulb. If this occurs, the cement on entering will adhere to the walls and vitiate the accuracy of the result. The flask, both before and after the operation, and before taking the readings, should, for a short time, be immersed in a jar containing water at the temperature of the laboratory.

The British Standard Specification requires, for the determination of the specific gravity of cement, an instrument which is a slightly modified form of the Le Chatelier-Candlot. Below the bulb it is marked at 99·5 and 100·5 c.c.; above, at 131, 132, and 133 c.c., its exact capacity thus being 133 c.c. Each c.c. is divided into twentieths. Instead of the liquid having to be adjusted to a definite level, as in the Le Chatelier-Candlot instrument, approximately 100 c.c. are introduced, the exact volume being read off after the immersion of the flask. This volume deducted from the final reading gives the volume of liquid displaced. Exactly 100 grammes of cement are taken for the determination.

**Fallacy underlying the Test of Specific Gravity.**—It is difficult to understand why this test has become so general, especially in this country. It is commonly supposed that the perfectly burned clinker has a higher specific

gravity than that which has been more lightly burned, and that the specific gravity of clinker less fully burned is higher than that of the yellow slack. Nothing can be farther from the truth. When taken fresh from the kiln, there is practically no difference in the specific gravity of any of the products, provided the carbon dioxide has been entirely expelled. This we have frequently tested in practice, and the following are the results of one set of experiments :—

Four samples were taken from one place in a kiln.

No. 1. A piece of yellow slack burned.

No. 2. A piece of perfect clinker.

No. 3. A piece of lightly-burned clinker, showing in places white spots of lime.

No. 4. A piece of slag-like overburned clinker.

These were ground up and the specific gravity of each was taken in a bottle, the liquid used being paraffin, the specific gravity of which was taken in the same manner.

No. 1. Specific gravity 3·16    |    No. 3. Specific gravity 3·20
No. 2.         ,,         3·17    |    No. 4.         ,,         3·19.

As carbon dioxide and water are absorbed from the air, the specific gravity gradually diminishes, an aerated cement will, consequently, give lower results than one newly ground from freshly-burned clinker. The specific gravity may, in fact, really be regarded as a measure of the amount of aeration a cement has undergone. A lightly-burned cement, or one containing underburned material, will absorb carbon dioxide and water much more rapidly and to a greater extent than one ground from entirely hard clinker. A low specific gravity may, therefore, for this reason indicate light burning, or the presence of underburnt material. It must, however, be remembered that the extremely finely-ground cement, so much of which is now coming into the market, is much more absorbent than that more coarsely ground, and it may thus, after the same amount of aeration, give a lower specific gravity. It has been suggested that previous to the determination the sample should be heated at a temperature of 100° to 150° C. This treatment would leave it practically unaffected. The water absorbed exists in combination with lime as calcium hydrate, and it is almost needless to add that neither this nor the carbon dioxide would be driven off at the proposed temperature. Another suggestion is to expel water and carbon dioxide by heating the sample to redness. From what has been said it is obvious that after this treatment the highest possible specific gravity would be the result and the test would be of no value. Most specifications require the specific gravity to be not less than 3·1, which can easily be attained, as we have seen, by very badly-burned cements which have been insufficiently aerated, and the specific gravity is really a matter of quite negligible importance.

# CHAPTER IX.

## CRUSHING AND GRINDING MACHINERY.

CONTENTS.—Introductory—Reciprocating Jaw and Gyratory Crushers—Fine Crushers—Crushing Rolls—Grinding by French Burr and Emery Millstones—Edge Runner Mills—The Ball Mill—The Tube Mill—The Kominor—Compound Mills—The Centrifugal Ball Mill and Fuller Mill—The Griffin and Bradley Mills—The Sturtevant Mill and Screen Separator—The Kent Mill—The Sieveless Ball Mill and Air Separator—The Albert Raymond Mill and Air Separator.

**Introductory.**—The first and last operations in the manufacture of Portland cement are those of grinding, as both the raw materials and the clinker from kilns require reducing to an extremely fine state of division. Since to produce 100 tons of cement clinker about 160 tons of raw material considered as in the dry condition are required, the question of the efficiency of the grinding plant is an important one. In addition to this, when the calcination is by rotary kilns the coal, equal to at least 25 per cent. of the weight of clinker produced, has, after drying, to be finely ground. Thus to produce 100 tons of cement by the rotary process, which is now becoming very general, 281 tons of material have to be ground.

From the beginning of the Portland cement industry the method of grinding was for many years almost entirely by the use of French burr millstones, the preliminary crushing being effected either by edge runner or roller mills, the latter of various types, the rollers being either plain, corrugated, or provided with teeth. At a later period, the use of Blake stonebreakers or other reciprocating jaw machines of this type became general. From the light stones and working parts of the cornmill, the heavy stones built of hard burrs, and the massive gearing of the cement mill were gradually evolved. In the early days when finely ground cement was not demanded, and when the clinker was not heavily burned, this system of grinding answered very well, as the cement was considered finished when it left the mills, without any subsequent sifting. With the demand for cement of greater strength, which could only be reached by more highly limed and heavily-burned clinker most difficult to grind, and with the necessity for more finely-ground cement, it was found that this system of grinding left much to be desired. At that time only the grinding of the cement clinker had to be considered, as the raw materials then in use being soft and easily broken down were treated in a different manner.

Repeated attempts were made to devise a better method of grinding than by millstones, and much money was spent in fruitless experiments before satisfactory results were reached. Many efficient machines are now in use, each type varying in its construction and details, according to the views of the makers. It will only be possible in this book to describe some of the most important of them. Whatever system of grinding is employed, preliminary crushing of the material is generally necessary, and machines for this purpose will be first considered.

**The Reciprocating Jaw Stonebreaker.**—Most of these machines are modifications of the original patent of Blake, these modifications consist generally of different methods for actuating the reciprocating or swing jaw, and they possess no real advantage. Fig 6 represents a section of a Blake
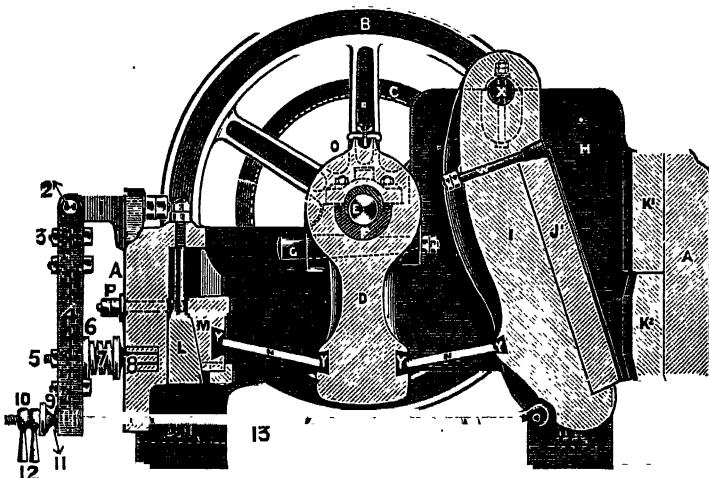


Fig. 6.—Broadbent's Blake Type Stonebreaker (Sectional View).

machine made by Messrs. Robert Broadbent & Son, Ltd. The main frame A, which carries every part of the machine, is cast in one piece, but in the case of machines for export to countries where transport is difficult it is built up in sections of steel plates bolted together; X is the swing jaw shaft, and I the jaw, K 1 and K 2 are the fixed jaw faces, and J the swing jaw face. These faces are either of a special mixture of hard iron or of manganese steel, and they are provided with vertical V-shaped grooves, which bite into or engage with each other. When worn at the bottom they may be turned end for end, when they are again serviceable for a considerable time. For the manufacture of road metal the grooves are large and deep, the object being to break the stone into cubes without crushing it more than is necessary, and to do this with a minimum quantity of small material and

dust. When, as in the case of cement manufacture, the object is to crush
the material, the grooves are made smaller. Thus, for cubing purposes,
the distance between the ridges is about $2\frac{1}{2}$ inches, while for crushing it is
usually about $1\frac{3}{4}$ inches, K 1 and K 2 are kept in place by the cheeks H, the
swing jaw face is secured by the wedge bolts W; E is the driving shaft, the
centre portion of which has an eccentricity of about 1 inch. This shaft is
provided with two heavy fly-wheels B and C, to either of which the driving
pulley may be bolted, and by lengthening the shaft a loose pulley may be
employed if necessary. The eccentric action of the shaft E, which is driven
at a speed of 250 revolutions per minute, imparts a swinging motion to the
pitman D, and this motion is transmitted by the toggle plates N N to the
moving jaw. This jaw approaches to, and recedes from, the stationary
face, and the material to be broken is charged into the hopper-shaped space
at the upper part of the jaws. It is thus continually struck, liberated, and
reduced in size as it passes downwards to the orifice at the bottom.
The width of this is regulated by the wedge block L, and the return of the
swinging jaw is effected by the drawback motion indicated by the numbers
1 to 13. Any attempt to obtain a very fine product at one operation by unduly
contracting the discharge opening will certainly result, sooner or later, in
the breakage of some part of the machine, probably the eccentric shaft. If
a finer product is required it may be obtained by the use of a second machine.
The crushed material passes from the first breaker to a rotary screen, formed
of perforated steel plates. The portion rejected falls between the jaws of the
second machine, which are set somewhat closer together than those of the
first, and in which the grooves may be closer together. The material is thus
roughly broken at the first operation, during which process a considerable
amount of dust and small is made. This having been removed by the screen,
the rejected portion, now of moderate size, renders possible the use of a more
closely set machine without risk of breakage. In some cases, as, for instance,
when only a small output is required, a fairly fine product may be obtained
from one machine. The product is screened, and the rejected portion, as it
is delivered from the end of the screen, is allowed to pass again through the
jaws, but the use of two machines is preferable.

   Fig. 7 is a sectional perspective view of Messrs. Hadfields' Blake type
stonebreaker. With the exception of the jaw faces and side cheeks, they
are made entirely of Hadfields' special toughened cast steel, the breaking
strain of which is nearly six times greater than that of cast iron. They are
made of about one-half the weight of the corresponding size machines of
cast iron, and even then are three times stronger. The jaw faces and the side
cheeks are of Hadfields' " Era Manganese Steel," which possess high wear-
resisting properties. These machines are made in 11 sizes, the mouth or
receiving opening ranging from $10 \times 6$ to $36 \times 24$ inches, the smallest
having an output of from 3 to 5 tons, the largest from 60 to 80 tons an hour,

the product passing a 2½-inch ring. There are two larger sizes, 42 × 30 inches, which will break from 100 to 150 tons an hour, and 54 × 36 inches, with an output of from 175 to 225 tons an hour, in both cases to 6-inch pieces. Both these machines are built in sections.
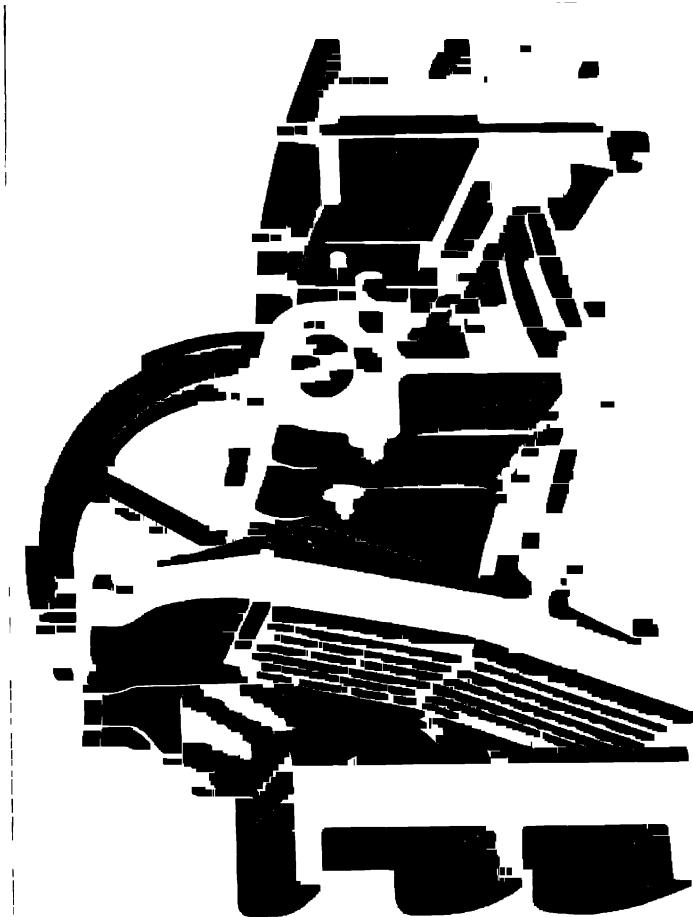


Fig. 7.—Hadfields' " Blake " Type Stonebreaker (Sectional Perspective View).

**The Gyratory Crusher.**—The crushing action of the pestle and mortar, when the pestle is simply rotated in the mortar and not used in the form of a stamp, has been taken as the model by more than one inventor for stonebreaking or crushing, as also for grinding purposes. Stonebreakers

and rough crushers constructed on this principle have long been in use in America, and, although employed to some extent in this country, they have never been popular here. Fig. 8 is a sectional view of a machine of this type made by Messrs. Hadfields, Ltd., of Sheffield, but it is necessary to understand that the crushing cone 6 does not simply rotate, but is caused to gyrate by the action of an eccentric motion applied to the lower end of
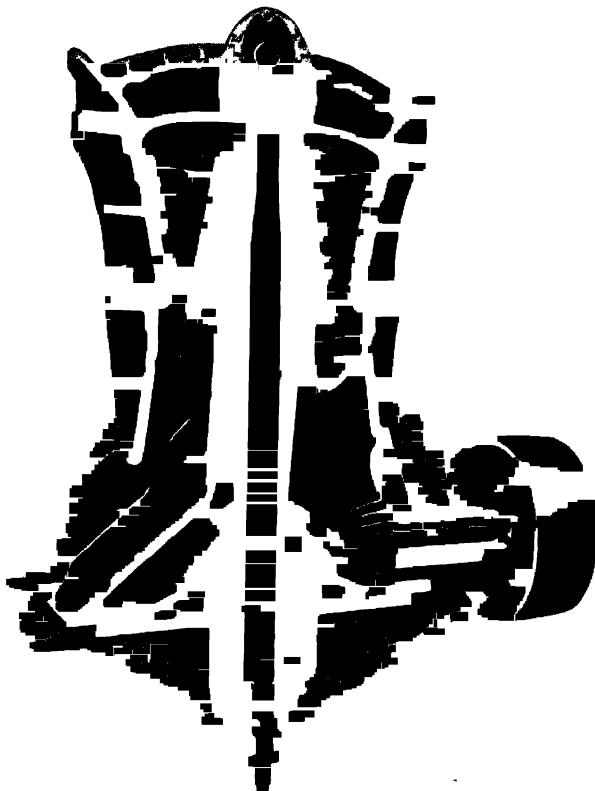


Fig. 8.—Hadfields' Gyratory Rock and Ore Breaker (Sectional View).

the hollow shaft to which the cone is attached. As it gyrates it approaches to and recedes from the concave shell, the distance between the cone and the shell, and, consequently, the size of the product may be regulated by means of an adjusting screw at the lower end of the shaft. The cone mantle 7, and the concave liners 27 and 28, are of Era Manganese Steel.

In comparing the gyratory crusher with the reciprocating jaw machine, it is clear that the efficiency, or output, will depend upon the quantity

which can be operated upon in any given period of time, and it is also evident that of these two machines that one will be the most efficient which brings into action the largest efficient crushing surface in the time in question. The diameter of the crushing cone of a gyratory breaker is about the same as the width of a reciprocating machine which would admit the same size of stone. As, however, the circumference is about three times the diameter, and as the cone makes one complete gyration for every forward motion of the swinging jaw, it is evident that three times the quantity of material can be dealt with by the gyratory machine in the same period of time as by the machine of the reciprocating type. Messrs. Hadfield make these machines with capacities from 4 to 150 tons per hour.

.The Hecla Disc Crusher, Symon's Patent.—This also is made by Messrs. Hadfields. It will take the material from a coarse crusher, either screened or unscreened, and reduce it at one operation to ¾ inch and less. Fig. 9 shows it in longitudinal section. Quoting from the makers' description :—*

" The crushing is done between two discs. They are saucer-shaped, and are set with their hollow or concave sides facing each other, thus forming a cavity between them. When stone is fed through the central feed spout, it is thrown by centrifugal force into the opening where the discs are widest apart. It is carried around with the discs to where they are close together, and is crushed in the operation. The smaller particles fly out from between the discs into the encircling shoot, while the larger particles are caught again and the operation repeated. These discs both rotate in the same direction at the same speed, and are supported at an angle to each other. This provides a wider opening between the edges of the discs at one part of their circumference than at the opposite part.

" The two discs A and B are held in place by two shafts, one of which is hollow and contains the other. The large ball and socket connection of the shafts allows their axes to be set at an angle to each other. The outer disc A is held in a cap firmly fastened to the bell-shaped end of the hollow shaft C, and is driven by the belt wheel D. The inner disc B, supported by the half-ball and solid shaft, inclines to rotate with the disc A, though not positively driven when the machine is running empty. When, however, stone is introduced between the discs they both rotate together in the same direction at the same speed affording the crushing action previously explained. This crushing action is quite independent of the eccentric E, and would be carried on if the latter remained at rest. This eccentric comprises the head of the pulley F, which is driven in a direction opposite to that of the pulley D. The function of the eccentric is to increase the rapidity of the crushing action or closing of the discs. In other words, the outer end of the solid lever shaft is carried around in one direction by the eccentric E, while both shafts are rotating together in the other direction. The two shafts and discs

* Pamphlet. Hecla Disc Crusher, Symon's Patent, Sheffield, June, 1915.

attached rotate at the proper speed to force the feed and fling out the product, while the rapidity of the crushing movement is increased by the eccentric to afford great capacity."



Fig. 9.—Hecla Disc Crusher (Symon's Patent).

The feed shoot is elliptical in cross-section to allow of the admission of flat pieces. The crushing members are completely enclosed by a casing divided vertically, each half being hinged to a supporting shaft. The crushing discs are of " Era Manganese Steel." The machine is made in four sizes. The largest, which admits pieces up to 6 inches, will crush from 50 to

60 tons an hour to pass a $1\frac{1}{2}$-inch ring, the smallest, admitting pieces up to $1\frac{3}{4}$ inches, will crush from 6 to 8 tons to pass a $\frac{1}{2}$-inch ring.

**The Sturtevant Open-Door Fine Crusher.**—In this machine the vertical spindle rotates without gyratory motion. It is illustrated by Fig. 10. The door opens like that of a safe, and exposes the whole interior rendering the
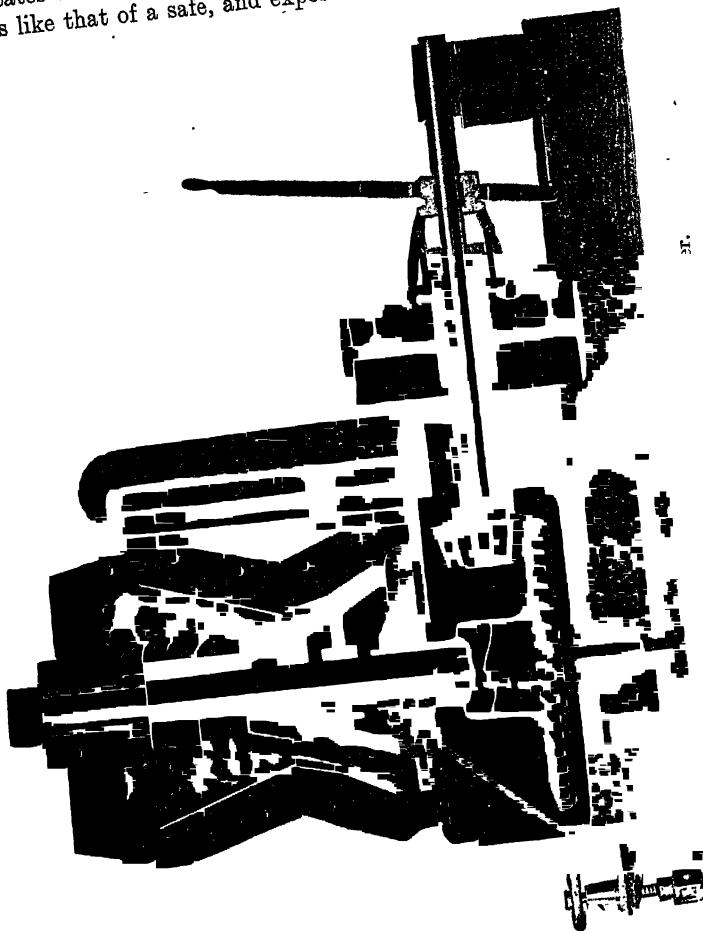


Fig. 10.

working parts, which are of moderate size and readily handled, accessible for removal, and replacement. The crushing cone can be raised or lowered to admit of either fine or coarse crushing, and can be adjusted to crush to a fineness of $\frac{1}{4}$ inch, and less. It can be arranged to deliver from any one of three sides, and is made in five sizes for outputs of from 1 to 25 tons

8

an hour, when crushing to maximum fineness. The makers do not advise its use for extremely hard rocks or for those containing much quartz.

**The Edge Runner Crusher.**—Although not generally used in the manufacture of cement, this crusher is of value in special circumstances and should be noticed. It is suitable for crushing coal, shales, and soft limestones. Fig. 11 illustrates the machine as made by Messrs. C. Whittaker & Co., Ltd., of Accrington. The pan revolves, the rollers turning on their axes. The bottom of the pan outside the roller track is formed of perforated plates. The material to be crushed is fed into the pan, and is guided underneath the rollers by adjustable scrapers. Centrifugal action throws the crushed material upon the perforated grates, the fine portion falls through
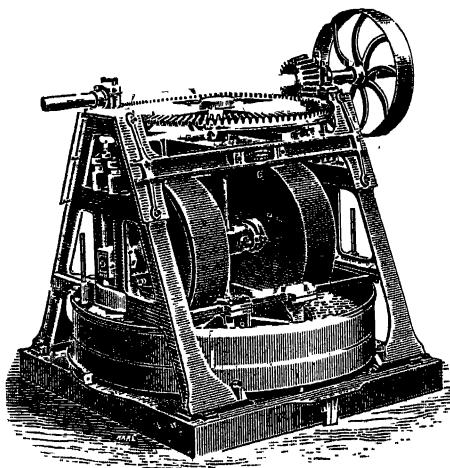


Fig. 11.—Whittaker's Edge Runner Crusher.

the perforations, while the coarse is led by scrapers to be further reduced under the rollers. The repetition of this action ensures a continuous supply of fine material. These mills are made with pans 6, 7, 9, and 11 feet diameter ; they revolve at speeds of from 28 to 30 revolutions per minute. When possible, the foundations should be so arranged that the product falls into a hopper below, from which it can be removed by a conveyor to an elevator. In default of this, under-scrapers must be provided to sweep it out, but their use involves a considerable loss of power by friction.

**Crushing Rolls.**—These are of two kinds—smooth, or toothed or corrugated. Smooth rolls are most suitable for the reduction of hard materials ; they will take the product from a coarse crusher and crush it finer. The relation between the size of the material fed to the rolls and that of the

product required should be about as 4 to 1. For example, roughly crushed material passing a 1½-inch ring will give a product which will pass a ¾-inch ring, including much small and dust. The fineness may be regulated by adjusting the distance between the rolls, for which suitable arrangements
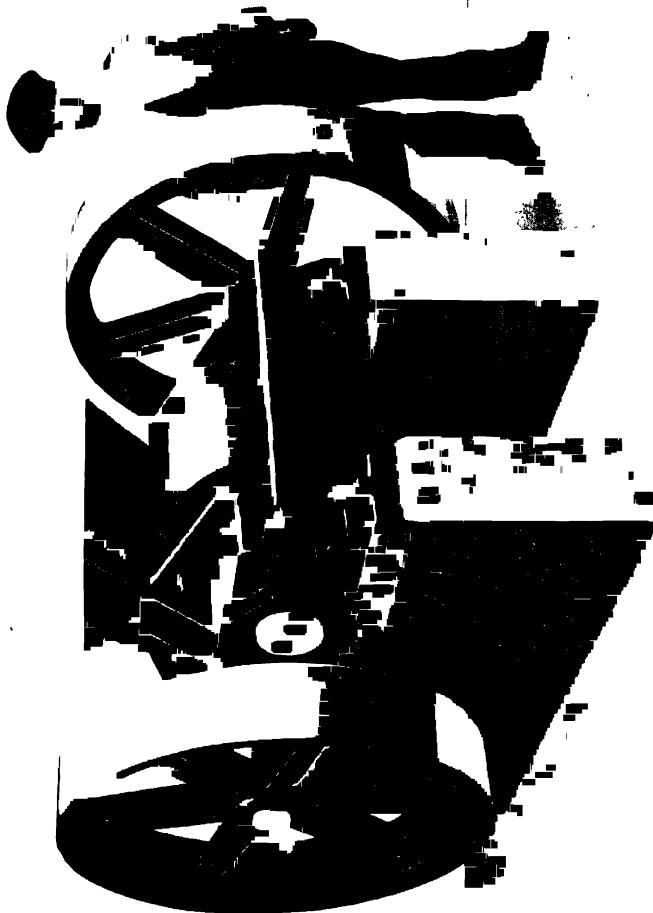


Fig. 12.—Hadfields' Smooth Crushing Rolls.

are provided. The feed should be regular and evenly distributed along the whole length of the rolls. The method of driving is either by gearing or belts. For moderate speeds gearing is employed, one roll driving the other by wheels with long involute teeth, to enable the distance between them

to be regulated. For higher speeds the driving is by a belt to each roll, one open, the other crossed. The rolls are formed by a core of cast iron to which shells of special hard metal or manganese steel are secured in such a manner as to be readily removed, and replaced, when requiring renewal.
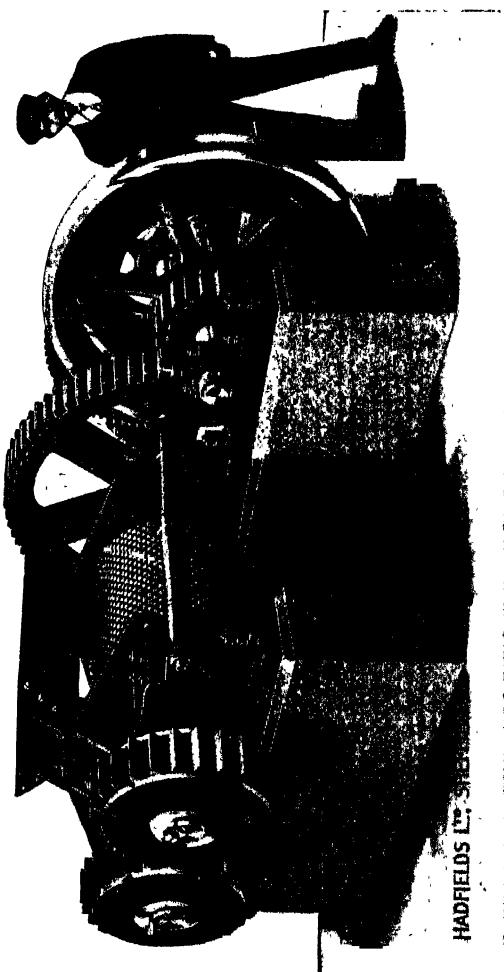


Fig. 13.—Hadfields' Toothed Crushing Rolls.

Toothed and corrugated rolls are adapted for crushing soft and moderately hard materials, such as shale, coal, and lime. They run at a low speed, and are always gear-driven. The form of the teeth is adapted to the nature of the material to be crushed. Both types are illustrated by Figs. 12 and 13.

**Grinding by French Burr Millstones.**—This system of grinding is, as regards new installations, now practically obsolete, but as preparatory
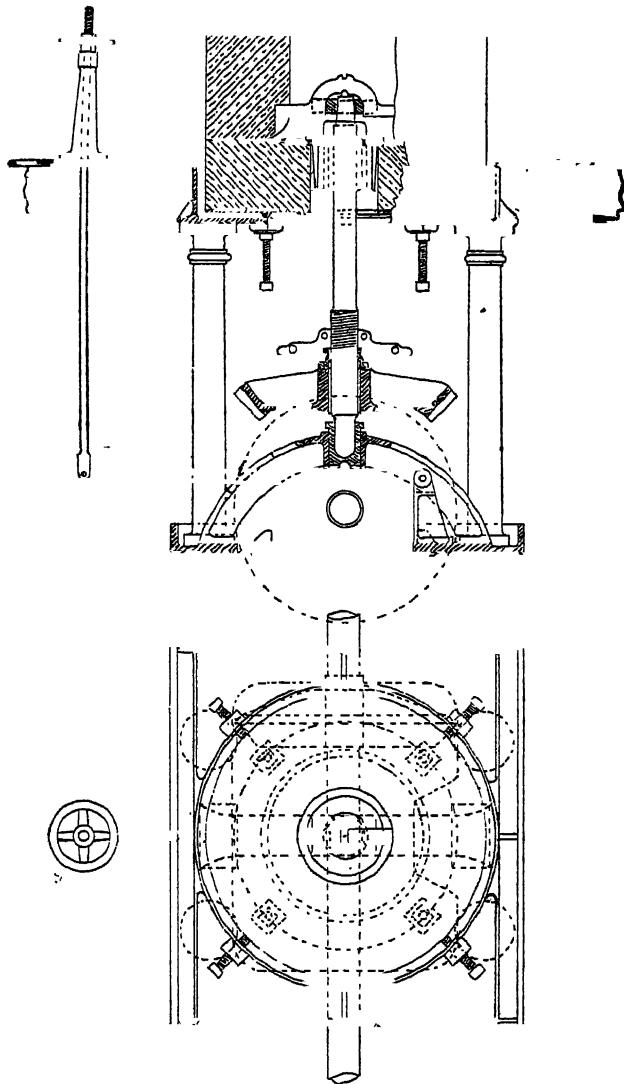


Fig. 14.—Millstones and Driving Gear—Sectional View and Plan.

or first-stage grinders for raw materials they can still be profitably employed, and their use may be briefly referred to. Fig. 14 is a cross-section

and plan of one member of a row of seven pairs driven from a lay shaft by nine 1¾-inch ropes direct from the flywheel of the engine. The stones make 140 revolutions per minute, and grind raw material, consisting of moderately hard limestone and shale as a preliminary to final grinding in tube mills. For this purpose they give very satisfactory results, the product containing much more impalpable powder than is usually found in that from other types of mill employed for a similar purpose, and, consequently, a larger output and a finer product is obtained from the tube mills. The construction of the gearing is extremely simple, is easily accessible, and is situated in a room below the working floor, away from dust. The wheels are in halves to facilitate removal, the pinions are adjusted, both for working and for lifting out of gear, by the hand wheels shown in the illustration. The lightering gear for adjusting the stones is actuated from the upper floor. The spiral conveyor for collecting the product from the separate mills is not shown in the illustration. It is placed close to the row of mills, and the cover of the trough is level with the floor ; it is thus easily accessible for examination, cleaning, and repairs. The stone cases, and the whole of the feed gear, are constructed of steel. It will be observed that in these mills, as is usual in English practice, the upper stone is the driven one or runner. On the Continent, and in America, mills of this type in which the lower stone is driven are used to a considerable extent, and are said to give better results than those with upper runners.

When visiting the Skanska Cement Works, near Malmo, in Sweden, a few years ago, one of the authors found that the whole of the raw material for a yearly output of 167,000 tons of cement was ground by millstones previous to final grinding in tube mills.

**Rock Emery Millstones.**—Millstones of French burr require redressing after 30 to 40 hours' use on hard clinker. The output begins to diminish long before they are thrown out of work for this purpose, and for the last few hours it is generally very small, while the power required to drive them increases. Messrs. Addison, Potter & Son, until recently Portland cement manufacturers on the Tyne, devoted considerable attention to millstone grinding, and built these stones of rock emery. They were constructed of segments formed in moulds in which the rough blocks of emery were fitted as closely as possible face downwards, the joints being run and the backs formed with specially hard cast iron. Provision, if required, was made for furrows by inserting pieces of French burr, which, from time to time, could be cut away, but for most purposes the stones worked very well without them.

The surfaces of emery stones do not polish, and they will work effectively during their whole life, which is much longer than that of stones built with French burrs. Of course, the surfaces cannot be touched with any tool, but, as a matter of fact, they do not need any dressing or levelling. It

is only necessary to put them out of work when it is required to attend
to the neck of the spindle, to lower the cross bar in the runner, or to cut away
the centre part of the bedstone and the swallow of the runner, for which
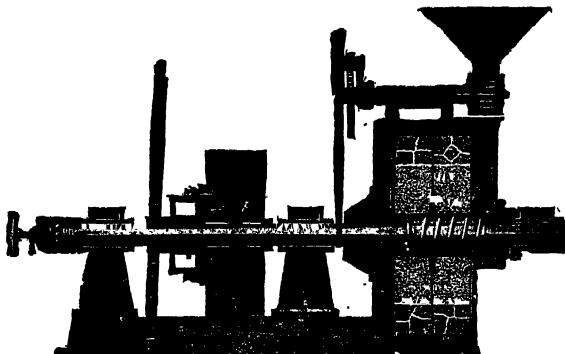


Fig. 15.—Sturtevant Emery Mill—Vertical Type.
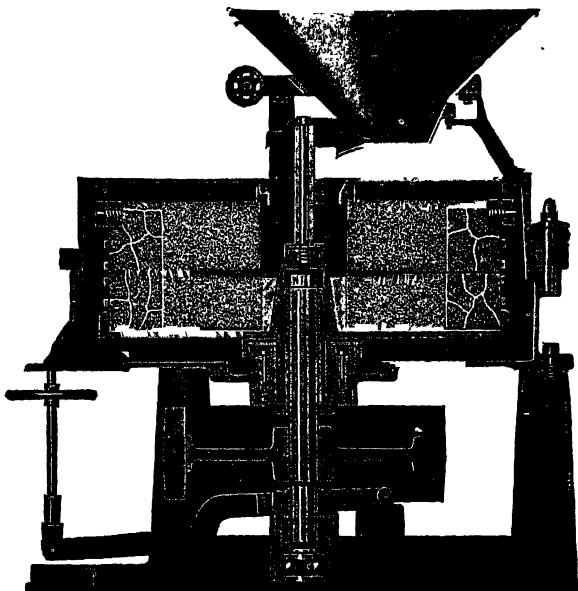


Fig. 16.—Sturtevant Emery Mill—Horizontal Type.

purpose these parts are constructed of French burrs. Our own experience
with these millstones, both for grinding cement clinker and raw flour from
hard limestone, was entirely satisfactory. Messrs. Potter employed them

both for single-stage grinding, and for double-grinding cement clinker to a high degree of fineness. For double-grinding the clinker was first very finely crushed, then passed through the first set of mills, which ground it so fine as to leave a residue of from 5 to 10 per cent. when tested on a sieve of 2,500 meshes to the square inch, finally, without any attempt at sifting, through the finishing stones which were specially built for fine grinding.

**The Sturtevant Emery Mills.**—These are constructed with the stones running in both vertical and horizontal planes. The horizontal type is designed for dealing with harder materials than the vertical one, and the lower stone is driven. They run at high speeds for mills of this type, the 42-inch vertical at from 450 to 500 revolutions, the 42-inch horizontal at 350 revolutions per minute. They are fine grinders, and the output is large, but they



Fig. 17.—Sturtevant Emery Millstone.

must be fed with very finely crushed material. These mills are used to a great extent in America for grinding natural cement. Figs. 15 and 16 show sections of both types, Fig. 17 illustrates one of the stones.

**Edge Runner Mills.**—Grinding mills of the edge runner type have been experimented with largely, and used in this country, but it is doubtful if they are now made to any great extent, if at all. Among them, Dutrulle & Solomon's Mill, Neate's Dynamic Grinder, Freeman's Hydraulic Grinder, and Duffield & Taylor's Mill have been those most extensively employed. Although not adapted for the fine grinding required at the present time, they are worthy of brief notice, as they did good work in their day, and the results obtained from them are of interest. They are capable of giving a much larger output than that shown by these results, of a product suffi-

ciently fine for finishing in tube mills, which will then comply with modern requirements, and, for this purpose, where still in existence, they may be profitably employed.

The Dütrulle and Solomon's Mill.—In this, the runners, four in number, revolve in different paths. The material to be ground is fed upon the upper one, and by the action of scrapers it is carried down to the lowest level from which it is delivered to an elevator. This conducts it to a sieve which separates the fine and coarse portions, the latter passing back again to be reground. The runners weigh about 6 tons each, and it is claimed that the grinding is effected rather by the rubbing together of the masses of clinker than by the contact with, and consequent abrasion of, the metal surfaces. It was found in the course of some trials that 40 I.H.P. was required to drive this mill for an output of 39¼ cwts. of cement in half an hour, or at the rate of about 10 I.H.P. per ton per hour. During this experiment the amount of material returned to be re-ground from a sieve of 150 meshes to the lineal inch was 40 per cent., with an 80-mesh sieve 24 per cent., and with a 50-mesh sieve 12½ per cent. The finished cement was ground to a fineness of 5 per cent. residue on the sieve of 50 meshes.

Neate's Dynamic Grinder.—In the dynamic grinder four rollers revolve round an inclined raceway. The clinker is in the first place crushed by powerful rolls, from which it is elevated to the storage bin, passing therefrom to the mill. From the mill, by means of a system of scrapers which form a special feature, it is delivered to two elevators. These discharge it into two rotating sieves, the wire cloth of which is protected on its inner surface by perforated steel plates. The fine portion of the ground material is carried away by screw conveyors, the portion rejected by the sieves passes back to the mill. The result of an extended trial gave a regular output of 5 tons per hour, the net I.H.P. required being 48·9, and the residue on sieves of 50 and 75 meshes being respectively 6·7 and 17·9 per cent.

The Freeman Hydraulic Grinder.—This consists of a bed or grinding plate, three edge runners of about 2 feet diameter by 10 inches wide, and an upper plate with a deep flange, all of chilled cast iron. The runners, by means of spindles and bearings, are attached to the flange of the upper plate which rests on them. This plate rotates at a speed of 50 revolutions per minute, and carries the runners round with it, travelling upon the bedplate upon which the material to be ground, crushed to pass a 1½-inch ring, is automatically fed. The flange of the upper plate shrouds the runners to a great portion of their depth, but, in addition, the whole mill is made dusttight by enclosing it in a sheet-iron casing, which may be easily removed for inspection and repairs. Upon the top and in the centre of the upper plate is fixed a small hydraulic cylinder and ram, by means of which the plate and runners are forced down upon the bed-plate and the material to be operated upon. The grinding is thus effected by the weight of the runners

and of the upper plate, supplemented by the hydraulic pressure, which may be regulated to suit material of any degree of hardness. By the action of the runners the material traverses the runner path to the circumference, it is swept out by a scraper and is carried automatically to a revolving sieve, the portion rejected being returned to the mill for further grinding. The driving is effected from beneath the mill, which may be supported on suitable columns, or it may be fixed on existing millstone hursts, the stones being removed. The output is stated to be 2½ tons per hour, the cement having 1 per cent. residue on a 50-mesh test sieve, and about 6 per cent. on a 76-mesh sieve, requiring from 30 to 40 I.H.P.

The Duffield and Taylor Mill.—In this machine the grinding path or pan revolves, the runners, four in number, revolving on their spindles. The outer bearings of these runners are maintained in position by standards fixed on the frame of the mill, in which they can slide freely in a vertical direction, downward pressure being applied to them by springs which can be adjusted to suit the hardness of the material under treatment. The inner ends of the spindles have ball-and-socket bearings, which, together with the springs on the outer ends, enable the runners to ride over any foreign or hard material that may accidentally get into the mill. An eccentric on the central shaft that carries round the pan imparts a lateral motion to the runners, which thus exert both a crushing and rubbing action on the material being ground. Scrapers fixed underneath the pan to its outer edge sweep out the ground material which is sifted; that rejected by the sieve being returned to the mill. These mills are constructed either to replace millstones, in which case the existing gearing and standards are used, or as separate erections which, if desired, may be driven from above.

The Ball Mill.—This was originally employed for fine grinding, for which purpose, owing to the small output, it was not a success. It is now chiefly used as a preparatory or coarse grinder, its product being finished in tube mills. In Figs. 18 and 19, the original mill, as made by Messrs. Jenisch & Lohnert, is shown in longitudinal and cross-section. The construction has been departed from in minor details, but the general principle is the same in all. The machine consists of a rotary drum built up of steel plates on a steel shaft of ample strength, a feed hopper being provided on the outer side. The sides are lined with renewable steel or chilled iron plates. It is made in a range of nine sizes up to 8 feet 6 inches in diameter, each size requiring a given weight of steel balls of various diameters. A few additional balls are added from time to time to replace loss by wear, as for the efficient working of the mill the specified weight of balls must be maintained. A mill having a drum 8 feet 6 inches in diameter and 5 feet wide revolves at a speed of 23 revolutions per minute, and requires 2½ tons of balls. The feed is continuous. The inner circumference of the drum is formed of heavy steel plates, perforated with ½-inch holes, the end of one plate is arranged to overlap
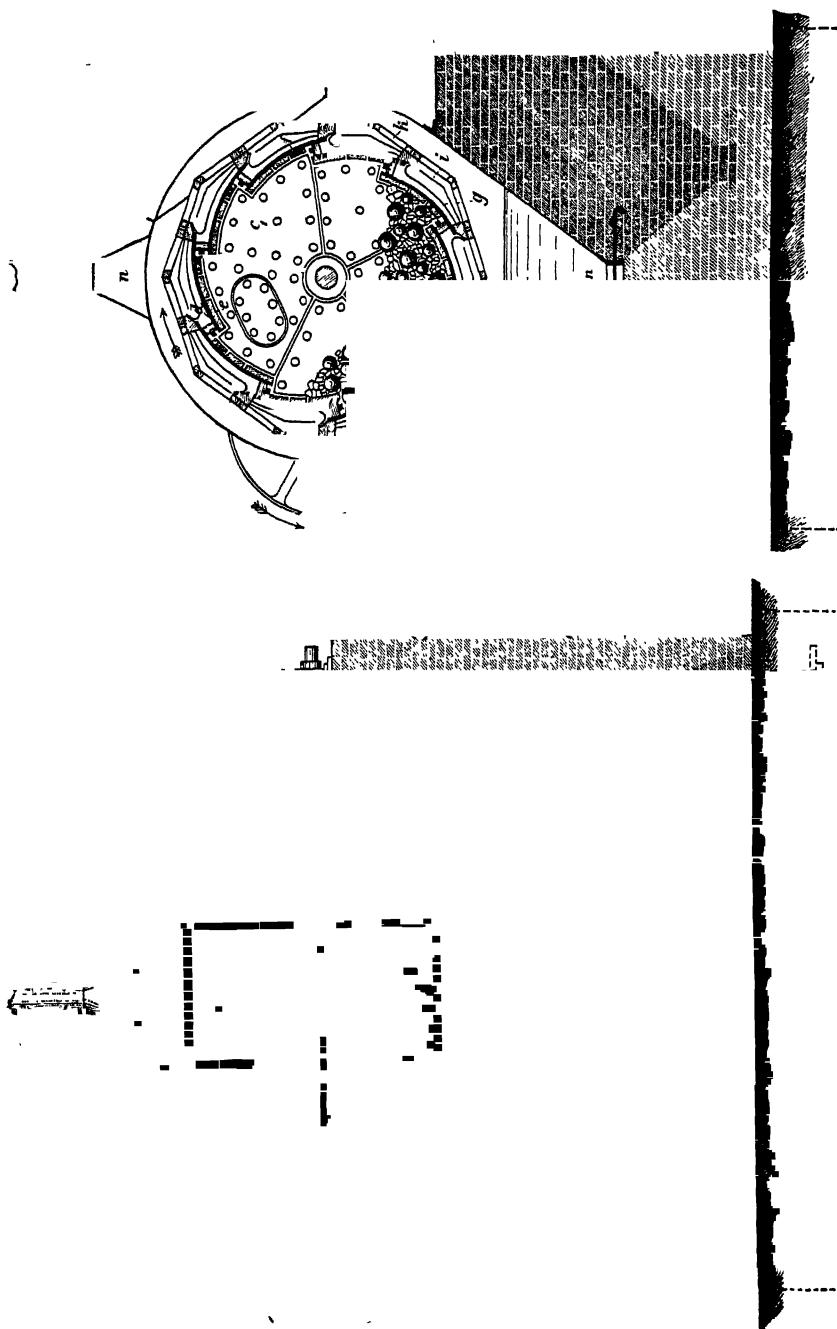
Figs. 18 and 19,—Jenisch & Lohnert Ball-mill—Type A.
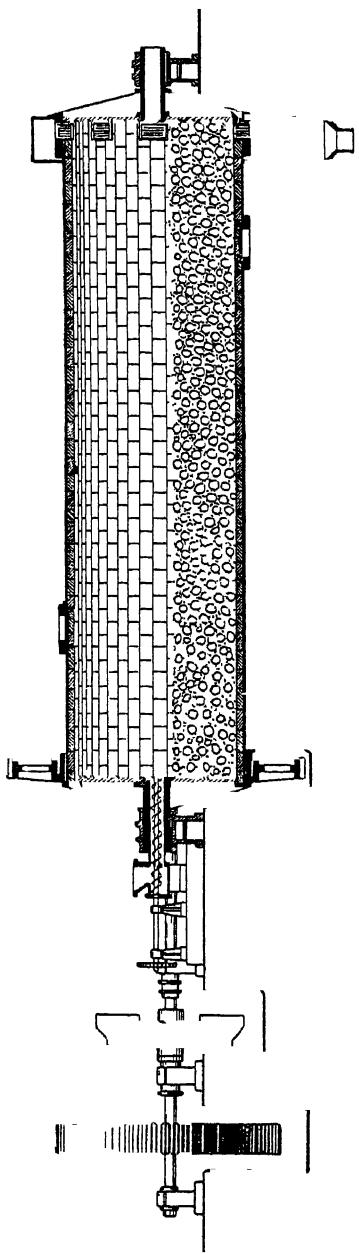
Fig. 20.—Tube Mill—Sectional View.

the beginning of the next one, with a space between them. This arrangement has the effect of diverting the balls from their rotary track as the drum revolves, and imparts to them a dropping motion, thereby increasing their crushing and grinding action. Surrounding the grinding plates is fixed a screen of perforated steel plates, which forms a protection for the outer or final sieves. These sieves, which are made of perforated metal, or brass or steel wire in accordance with the required fineness of the product, are constructed so that they can be easily replaced in case of damage. The material acted upon has first to pass through the holes in the grinding plates, then it must traverse the coarse or protecting sieve, leaving only dust and grit to pass to the outer fine sieves. The portions finally rejected by the sieves fall back into the centre of the drum, through the openings between the inner plates, for further grinding. The drum is enclosed in a dust-tight iron casing, and the ground material falls into a hopper below to be automatically conveyed away.

**The Tube Mill.**—This is a finishing or fine-grinding

mill for dealing with a product that has previously been coarsely ground by some other means; it was introduced to the cement industry in 1895. It was the invention of M. Davidsen, of the firm of F. L. Smidth & Co., and made rapid headway. At the present time nearly three thousand are at work in the cement works of the world; over fifteen hundred of these are of Messrs. Smidths' manufacture. The construction of the machine, which is shown in longitudinal section by Fig. 20, is simple in the extreme. It consists of a long tube or cylinder rolled from steel plates and welded at the joints, being thus entirely without seam or rivet. This cylinder is attached to cast-steel end-plates provided with hollow trunnions, on which it revolves in bearings lined with anti-friction metal. The feed is by a worm passing through the trunnion at the driving end of mill, either from storage bins or from a hopper containing a small reserve, sufficient to ensure steady feeding. The spur
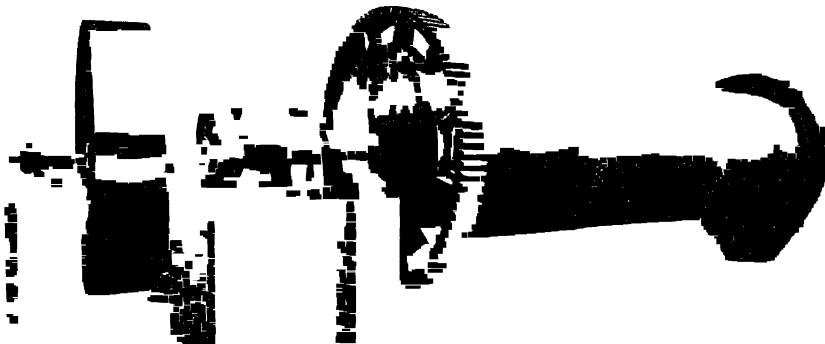


*F. L. Smidth & Co.*

Fig. 21.—Tube Mill—General View.

driving wheel is keyed to brackets cast on the inlet and plate. The lining may be of chilled cast-iron or steel plates, but quartzite or silex blocks are generally employed. They are from $2\frac{1}{2}$ to 3 inches thick, are roughly shaped in brick form, and are fixed with magnesium oxychloride current. This is prepared from lightly calcined magnesite, which is finely ground and mixed when required for use to a mortar of suitable consistency with a solution of magnesium chloride. The quartzite lining has a long life, much longer than that of steel plates. The mill is about half-filled with flint pebbles, which are hand-picked to assorted sizes, No. 1 from 1 to $1\frac{3}{4}$, No. 2 from $1\frac{3}{4}$ to $2\frac{1}{2}$, No. 3 from $2\frac{1}{2}$ to $3\frac{1}{4}$ inches in diameter. Generally, for dry grinding, the best results are obtained from the smallest sizes, but they soon become too small for profitable use, and many users prefer the medium size, $1\frac{3}{4}$ to 2 inches. As the mill revolves, the pebbles alternately rise and fall, the grinding being effected by their crushing and rubbing action as the material

operated on travels along the cylinder. Loss by wear is made up by the occasional insertion of more pebbles. Delivery of the ground material is arranged for by the provision of a narrow grid continued round the circumference of the mill at its extreme end, which is enclosed by a dust casing. The fineness of the product is controlled by the preliminary grinding, which should be at least so fine that all will pass a sieve having 400 meshes to the square inch. There is practically no limit to the fineness of grinding that may be obtained by the use of the tube-mill, either by finer preparatory grinding, by reducing the feed, or by the use of successive mills. Fig. 21 is a general view of the mill, which is made in nine standard sizes. Only the five largest of these, of which the following are the leading particulars, are employed in the cement industry :—

| Size. | Inside Diameter of Tube. | | Inside Length of Tube. | | Weight in Tons of Pebbles. | Revolutions per Minute. |
|---|---|---|---|---|---|---|
| | Ft. | Ins. | Ft. | Ins. | | |
| 20 | 6 | 5 | 24 | 4 | 14 | 23 |
| 17·5 | 6 | 0 | 20 | 0 | 10 | 24 |
| 16 | 5 | 5 | 20 | 0 | 8 | 25 |
| 14 | 4 | 9 | 18 | 7 | 6 | 27 |
| 12 | 4 | 2 | 15 | 9 | 4 | 29 |

Messrs. F. L. Smidth & Co. have calculated that in the largest mill there are about 175,000 pebbles.

The tube mill is suitable for both dry and wet grinding. Deviations from the original design have been made by other makers, these consisting principally in the method of delivery, which is sometimes arranged through the end trunnion, or in the end plate itself. The general practice of both English and American makers is, instead of welding the shells, to rivet them with butt joints and straps.

Messrs. Ernest Newell & Co., Ltd., of Gainsborough, make a tube mill, with steel balls as grinding bodies, for use as a preparatory grinder for pebble mills. They are of very strong construction, and are lined with steel plates. In length they are about half that of the mill they are intended to supply, but of greater diameter, the smaller sizes about one-third greater, increasing to one-half in the larger ones. They are suitable for both wet and dry grinding. The Allis Chalmers Company, of Milwaukee, U.S.A., have recently introduced a new form of ball for grinding mills, " The Concavex." Each ball is provided with two cup-shaped recesses of the same radius as the balls arranged opposite to each other. When in action the balls are said to interlock, thereby giving a larger surface contact area, and greater efficiency. We think that with continued use these balls will tend to wear flat.
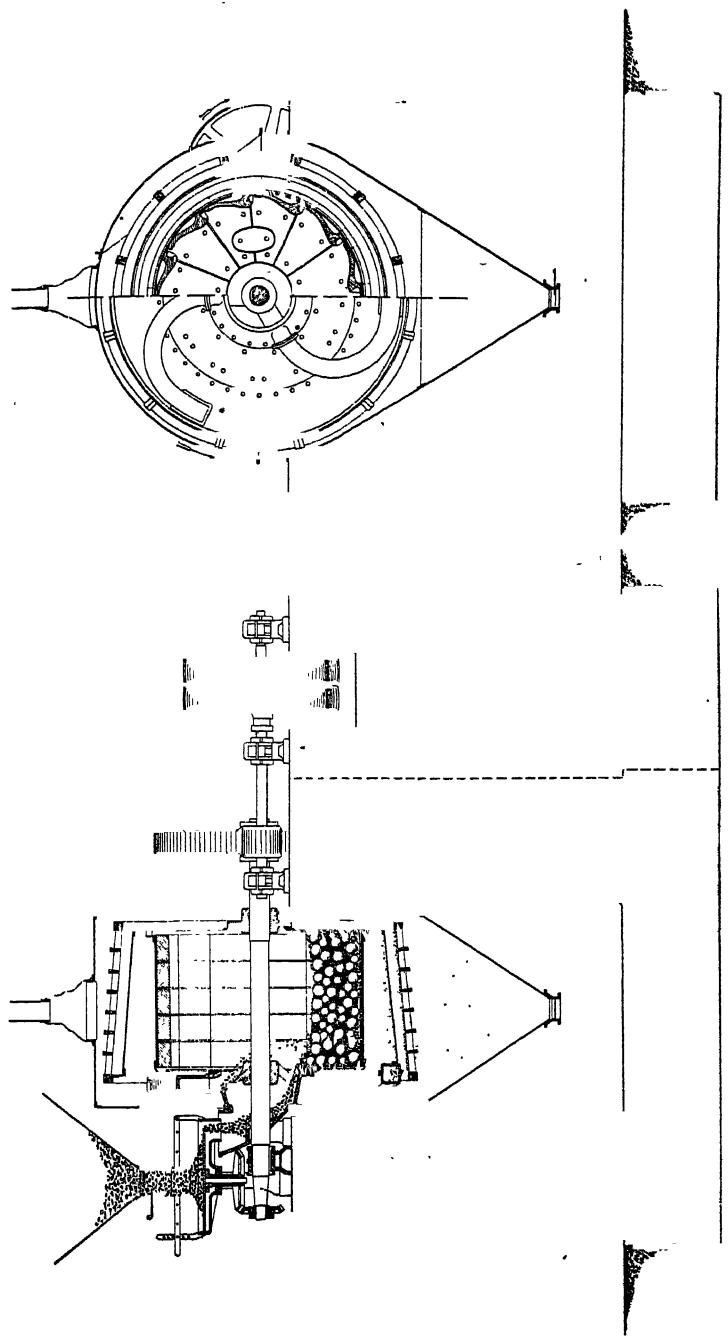
Fig. 22.—Kominor—Sectional View with Encircling Sieve.

**The Lindhard Kominor.**—This is a ball mill of an improved type, especially designed as a preliminary grinder for the tube mill. It is made by Messrs. F. L. Smidth & Co., and is known under the registered name of " Kominor." Fig. 22 is a sectional drawing of the original design. Instead of a built-up construction, as in the ball mill, the shell consists of a riveted cylinder of steel plate with steel-plate dished ends, and it is lined with cast-steel plates. Those on the circumference are not perforated, they are stepped as in the ball mill, but overlap each other closely without a space between them. As in the ball mill, the effect of this construction is to divert the balls from a rotary track and to impart to them a falling and crushing action. The material to be operated on is fed through one end of the drum, and has to travel along it exposed to the action of the balls until it reaches the opposite end, in which is situated the outlet. It here falls into the cone-shaped encircling sieve and travels back to the inlet end, the material passing the sieve falling into the dust casing for removal, that rejected being returned by three scoops to the interior for further grinding.

In the ball mill the action of the falling balls gradually closes the holes in the grinding plates, resulting in a continued decrease of output, while the sifting area is 50 per cent. less than that of a Kominor of the same size. A comparative test on limestone between a Kominor and a ball mill of equal size was made at a cement works in the Lehigh Valley, Pennsylvania. The limestone was first roughly crushed by a gyratory crusher, some of the pieces fed to the mills being as much as 3 or 4 inches in diameter. The Kominor ground 14,000 lbs. per hour against 8,000 lbs. produced by the ball mill, both ground to the same degree of fineness and with no apparent difference in the expenditure of power.

The first Kominors made were of moderate size, the largest only carrying 23 cwts. of balls, and for these the encircling sieve was found satisfactory. With increasing size—the largest carries 5 tons of balls—the sieves proved insufficient, and were also rapidly destroyed by the attrition of the coarse grit, even when protected by an inner screen of perforated plate. Replacement was frequently required, this work involving much time and loss of output, while when renewing the lining plates, although provision was made for passing them through manholes in the ends, they could not be unfastened without removing the sieves to unscrew the nuts from the bolts securing them to the shell. These difficulties were overcome by the introduction of the Fastax sieves. They are cylindrical and of small diameter, three being provided in the smaller mills, six in the larger ones. They give a much greater and more efficient sifting area, are easily accessible, and it is said that one can be taken out and replaced in twenty minutes, while by simply removing the dust casing the lining plate bolts can be unscrewed. At a moderate cost, these sieves can be adapted to machines of the earlier type, and this is often done. Fig. 23 is a sectional drawing of a Kominor with
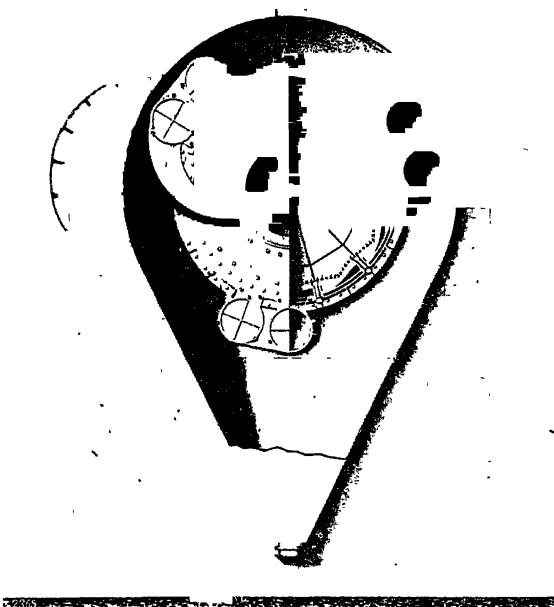
*F. L. Smidth & Co.*

Fig. 23.—Kominor—Sectional View with Fastax Sieves.



Fig. 24.—Kominor—General View with Dust Casing removed.

Fastax sieves. Fig. 24 is a general view with the dust casing removed. Fig. 25 shows the automatic revolving feed table, which is driven from the Kominor shaft. The cone of material from the hopper, which can be regulated by raising or lowering the sleeve, is cut off by an adjustable scraper in a



F. L. Smidth & Co.
Fig. 25.—Automatic Feed Table.

regular stream and delivered into the inlet of the mill. This is a most efficient and accurate method of feeding, which can be applied to many types of grinding machine.

**The Compound Mill.**—In this mill, the operation of grinding in two stages by steel balls followed by pebbles is effected in a single tube of uniform diameter divided into two chambers. As made by H. Lohnert in five sizes, with outputs ranging from 2 to 6 tons per hour, the length of the pregrinding chamber, which is lined with steel plates, is 9 feet, while that for finishing, which may be lined with either steel plates or quartzite blocks, is 16 feet. It contains flint pebbles. These dimensions are maintained in all sizes, the diameter being adapted to the required output, that of the largest size being 71 inches. The two sections are divided by an arrangement of diaphragms which separate the portion not sufficiently fine for the finishing chamber. By means of a steel plate casing surrounding the tube, the coarse is returned to the inlet end to be further acted upon by the steel balls, while that sufficiently fine for finishing passes through the diaphragm.

At the inlet end the construction and method of driving is exactly as that of a tube mill. The crushed material is fed through the hollow trunnion. At the delivery end the trunnion is dispensed with, the tube at some little distance from the end being encircled by a tire which bears on friction rollers. The outlet for the finished material is arranged in the end plate.

**Grinding Bodies, other than Flints, for Use in Tube Mills.**—By the use of ball and tube-mill the operation is one of two stages. Messrs. F. L. Smidth & Co. extended it to three stages by dividing the tube-mill into two chambers by a diaphragm, retaining the pebbles in the chamber at the inlet end and replacing them in the other end by small steel cylinders, which they describe as "Cylpebs." The effect is either to obtain a larger output than from pebbles alone, of the same fineness, or an equal one of much greater fineness. The method has been adopted to a considerable extent, and is apparently simple, but to obtain satisfactory results considerable experience is required in the arrangement, and for exact details the inventors should be consulted. The position of the diaphragm, and the weight of cylpebs introduced, must bear a certain relation to the dimensions of the mill, the nature of the material to be ground, and the required fineness of the product.

Hollow cylinders of malleable cast iron, about 1¼ inches long and ¾ inch in diameter, known as "Holopebs," have also been used in tube mills, entirely replacing pebbles, giving either a larger output of the same fineness or a finer one for the same output. Experience proved that they were liable to break up in mills with a peripheral discharge, while in those discharging through the trunnion this was not the case. In consequence of the difficulty of obtaining these castings during war-time, and their non-applicability to each type of discharge, experiments were made to overcome these difficulties, resulting in the production of "Helipebs." These are made of steel wire coiled in the form of a helix, and afterwards hardened by a special process. Their usual size is 1¼ inches long by ¾ inch external diameter, and about 1¼ ounces in weight, but they can be made of any size,

adapted to the material to be treated and the required fineness of the product.

While helipebs will give good results in mills with either trunnion or peripheral discharge, the best are obtained from the latter, but this is equally true of pebbles. The grinding surface in proportion to the weight is many times greater than that of pebbles. The loss in weight is given as 1 ton for every 6,000 tons of cement ground. It might be supposed that in action they would lie horizontally and roll over each other, but this is not the case. They arrange themselves vertically, and, being hollow, carry up while rising a portion of the material operated on, which, as they fall, is distributed between the grinding surfaces. Helipebs may be used in either steel plate or quartz-lined mills. They are illustrated by Fig. 26.
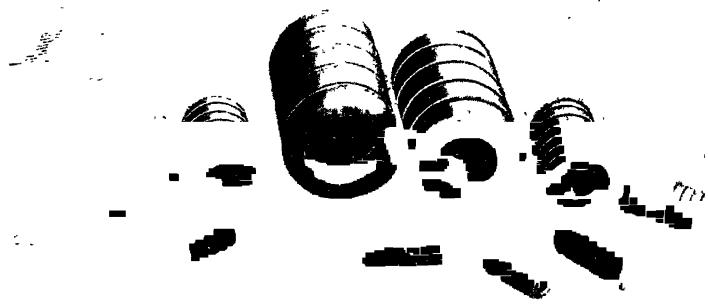


Fig. 26.—Helipebs for Tube Mills.

**The Centrifugal Ball Mill.**—The original type of all these mills was the Morel. It has undergone many modifications and improvements, but the general principle is the same in all. Three or more steel balls are driven round a concave steel ring in either a vertical or horizontal plane by centrifugal action against the ring, as is also the finely crushed material to be ground. This is reduced against the ring by the action of the balls until it is sufficiently fine to be removed from the mill by a sieve. This mill has been used to a considerable extent in France, especially at Grenoble, for grinding natural cement.* A recent modification called the " Roulette " has been introduced to the Portland cement industry as a fine grinder, and is said to be very successful. The centrifugal ball mill now to be described has had a widely extended use.

* _Étude sur le fabrication et les propriétés des ciments de l'Isère._ M. A. Gobin. Dunod, Paris, 1889.

**The Fuller-Lehigh Mill.**—This is illustrated by Figs. 27 and 28. The grinding is done by four steel balls, which are propelled round the grinding ring by four equidistant arms radiating from, and attached to, the central shaft. The feeding device is clearly shown by the illustration. The material to be ground, none of which should exceed $\frac{1}{2}$ inch in size, falls between the balls and the grinding ring, and is at once reduced to powder. The upper

FEED INLET

FEEDER DRIVE

FEEDER

CE

MIL
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PUL

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CT
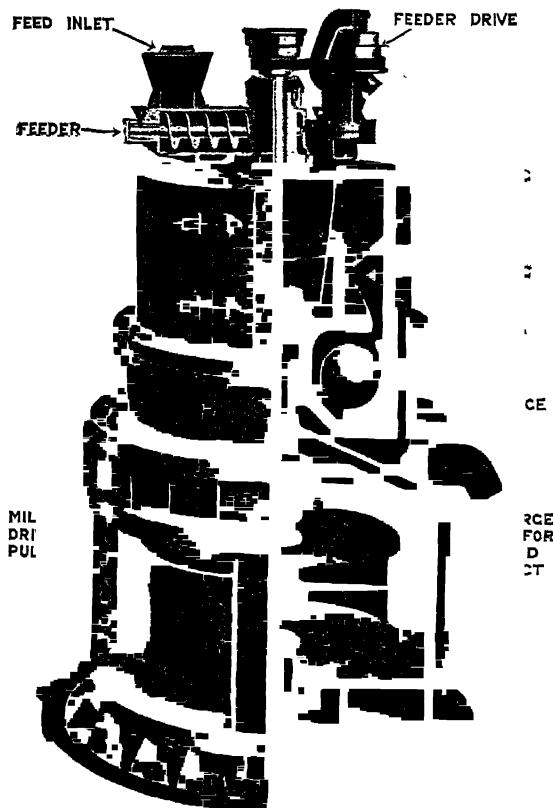
Fig. 27.—Fuller-Lehigh Centrifugal Ball Mill.

section of the mill is enclosed by a double screen. The outer or finishing one is of woven wire cloth of mesh suitable for the required fineness of the product, the inner one serves as a protection to prevent damage by flying fragments, or the action of coarse grit, on the cloth. The material rejected by the screens falls into the grinding chamber for further reduction. The mills are provided with two fans, an upper and a lower one. The upper

fan lifts the partially ground material from the grinding zone into the upper chamber and keeps it in suspension, the lower one acts as an exhauster and draws the portion, ground sufficiently fine, through the outer sieve into the space between this and the outer casing. It is collected on a sweep, which is keyed to the main shaft, and discharged by a spout.

The mill may be driven either by belt or bevel gearing, or by a directly coupled motor. Fig. 29 shows the last-mentioned arrangement. The motor is suspended in a well-ventilated concrete pit accessible from the outside of the building. The shafts of mill and motor are separate pieces connected by a coupling, so that either machine may be removed without disturbing the other. The mill is made in four sizes with grinding rings 24, 33, 42, and 47 inches in diameter.



Fig. 28.—Fuller-Lehigh Mill—View of Grinding Chamber and Fans.

**The Centrifugal Roller Mill.**—This type of mill consists of from one to four rollers freely suspended on spindles, which by centrifugal force are carried round against a fixed grinding ring. They are sometimes described as pendulum mills. By the action of a fan, the product when sufficiently fine passes out of the mill through a sieve, that rejected by the sieve falling back for further grinding. The Griffin & Bradley mills, which have had a very extended use, are the best representatives of this class.

**The Griffin Mill.**—The principle of the action of this mill is thus explained by its inventor :—*

" The principle of grinding used by the Griffin mill is that of a roll running within and against an annular die, being held in operative contact by centrifugal force. Other mills employing this principle have been made, but

* From a paper by E. C. Griffin read before the Association of American Portland Cement Manufacturers. June, 1905.
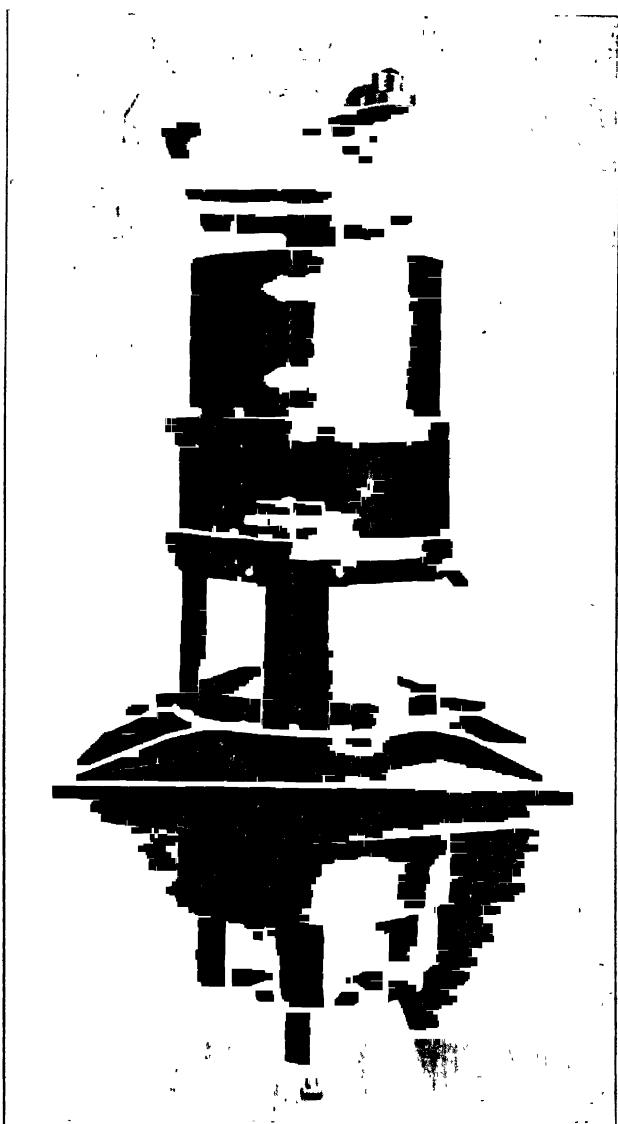
Fig. 29.—Fuller-Lehigh Mill driven by Direct-coupled Motor.

no other mill of this kind is largely used to-day for this purpose, and none is used at all which does not employ some of the details of construction designed in the first place by the inventors of the Griffin mill.  One reason
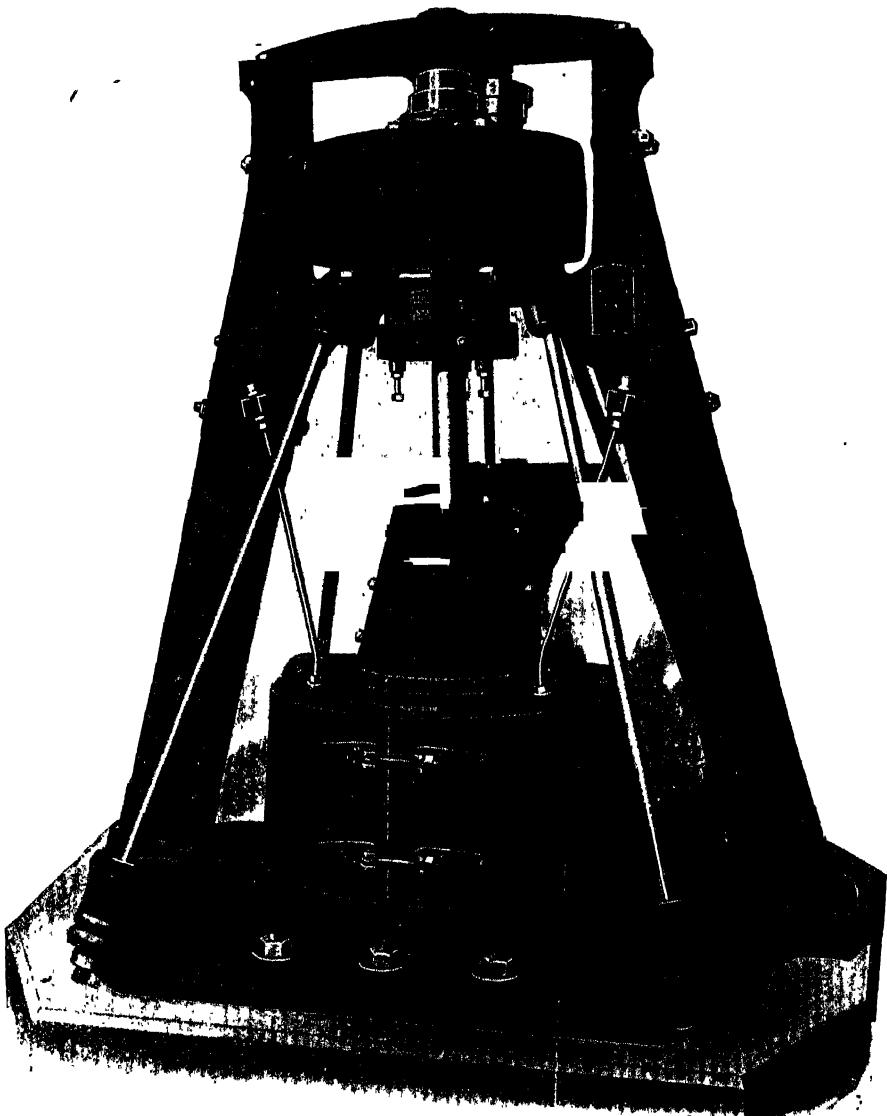


Fig. 30.—Griffin Mill with Composite Frame.

for the failure of other roller mills, and the success of the Griffin mill in grinding Portland cement, is that the roll of the Griffin mill acts on the material in the mill in a way different from that of any other mill.
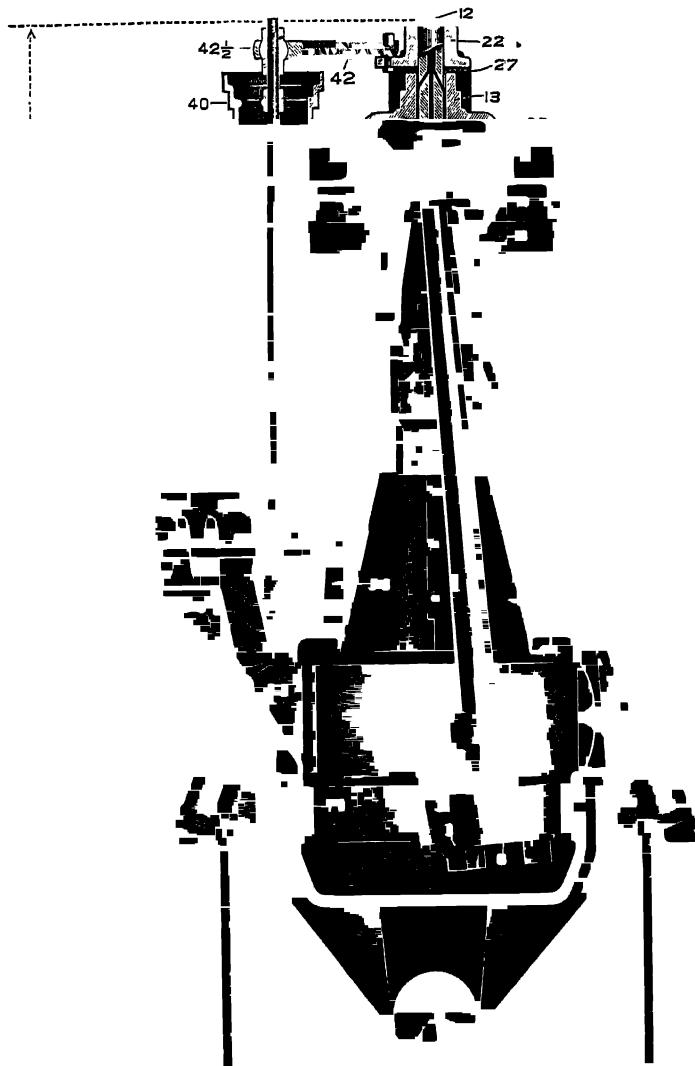


Fig. 31.—Griffin Mill—Sectional View.

" This peculiar action is effected by the positive rotation of the roll, by means of which it pulls itself around the die or ring, on which it runs and operates, and has a drawing action on the material, pulling it, so to speak, between the roll and the die, and exerting a crushing and abrading action which no other machine does. Its efficiency is further increased by the fact that all journals are removed from the grinding chamber. This point is of especial importance in machines used for grinding Portland cement, as owing to its great toughness an unusual amount of heat is developed. The machine necessarily becomes very hot, and this heat is destructive to lubricated bearings.

" The principle of driving the roll in the Griffin mill is a peculiar one. It has puzzled many who have examined it, and has appeared paradoxical to many, owing to the fact that the pulley and the roll, being axially connected, must of necessity revolve in the same direction and with the same angular velocity, and yet the roll runs round the die in a contrary direction to the pulley, and with a greater number of revolutions per minute than the pulley. In the mill, as ordinarily constructed, the pulley of the mill runs left-handed, or against the sun, at 200 revolutions per minute, while the roll will travel right handed around the die at the rate of about 300 revolutions per minute. These peculiar and apparently paradoxical motions and variations in speed are, of course, easily explained upon a critical examination, but to the casual observer they seem quite wonderful."

The universal joint by which the shaft is connected to the pulley allows perfect freedom of movement to the roll, so that it can easily pass over obstructions of any kind. Pieces of iron or steel thus do no damage to the mill. The feed is continuous through the hopper 50, by means of the worm 49 which is driven by the step pulley 40 that regulates the rate of feed. The mill will deal with material as crushed by a stonebreaker, but passing a ¾-inch ring. As soon as the mill is in full operation, and when sufficient material has entered the pan, it is stirred and kept in rapid motion by the action of the shoes on the bottom of the roll, which throw it between the grinding ring and the roll. The fine powder, as fast as it is produced, is removed through the screen by the fan 7, which draws air from the top to the cone 25, the dust falls into the conveyor channel below. The mill thus continuously grinds and sifts within itself. The screen may be of much coarser mesh than the finished product. One having 16 divisions to the lineal inch will, for instance, deliver a product leaving less than 10 per cent. of fine residue when tested on a sieve having 60 meshes to the lineal inch. The mill is self-contained, being entirely built on the bed-plate, and by some modifications may be adapted for wet grinding. The grinding ring is 30 inches in diameter, the pressure of the roll against it being 6,000 lbs. The output on hard cement clinker may be from 1½ to 2½ tons per hour, according to the fineness required. It was originally made with a heavy

cast-iron frame.  It is now of composite construction, the wooden standards resting on rubber blocks, thus giving a large measure of elasticity to the
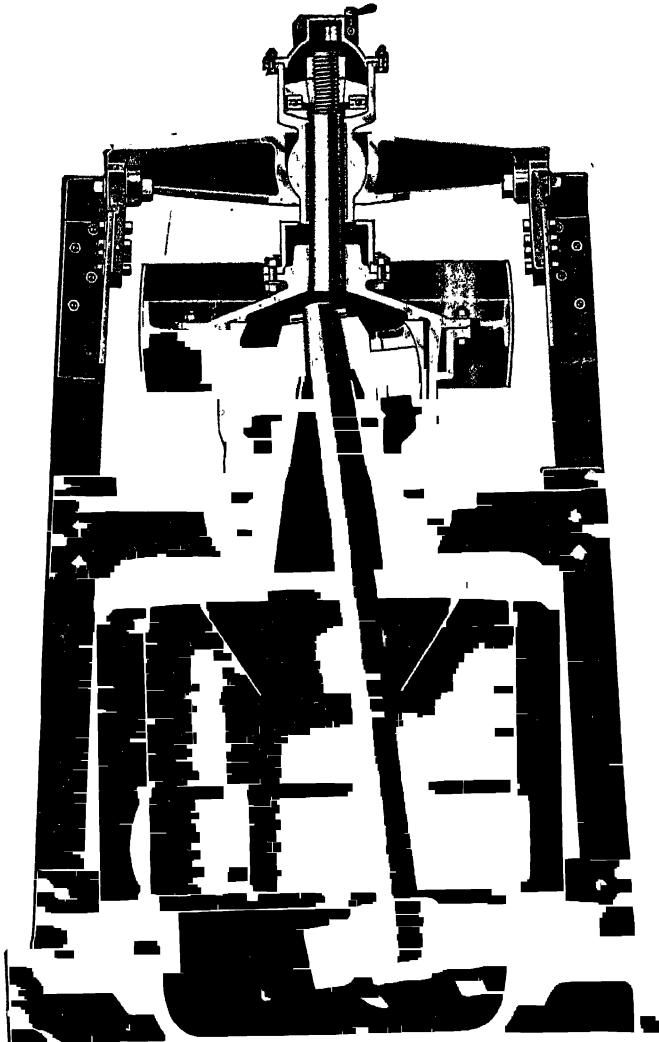


Fig. 32.—Giant Griffin Mill—Sectional View.

framework, and cushioning the severe vibratory strains which are necessarily set up in a machine of this kind.

Fed with material of $\frac{3}{4}$ inch and under, this mill will grind from 2 to

2¾ tons per hour of rotary clinker, of limestone 4 to 6 tons, each to a fineness of 84 per cent., passing a sieve of 200 meshes to the lineal inch, the I.H.P. being from 80 to 85. On coal from 4 to 5 tons an hour to a fineness of 95 per cent., passing a 100-mesh sieve, the power being slightly less than in the previous instances.
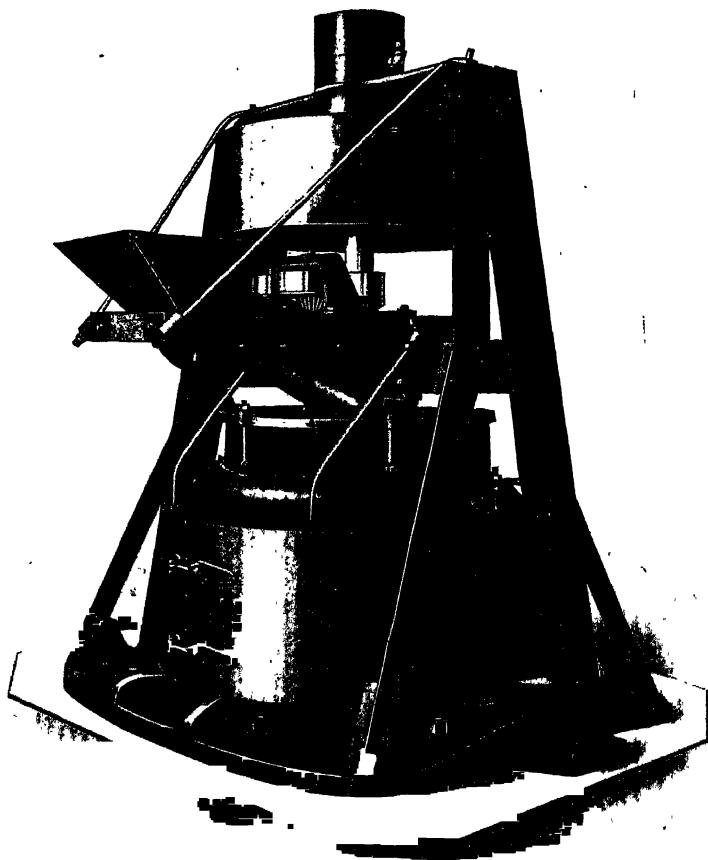


Fig. 33.—Bradley Three-Roll Mill.

**The Bradley Three-Roll Mill.**—This is illustrated by Fig. 33. The grinding is effected by three rolls acting against an annular ring, the material to be ground, none of which should be larger in size than ¾ inch, being delivered against the ring directly in front of the advancing rollers. The weight of the grinding mechanism is carried by the vertical driving shaft, which, by

a special arrangement, is caused to rise and fall while running, thereby relieving the footstep bearing of the dead weight, and, consequently, reducing friction, while the rubbing motion of the rollers against the ring, in addition



Fig. 34.—Bradley Hercules Mill.

to their rolling motion, increases the grinding effect. The diameter of the grinding ring is 3 feet 6 inches, the mill requiring 35 to 40 I.H.P. One of

these mills was recently grinding 3 tons per hour of hard burned shaft kiln clinker to a fineness of 12 per cent. residue on the 180 sieve for 38 I.H.P.

**The Bradley Hercules Mill.**—This is a preliminary grinder for preparing material to be finished by a tube mill. The diameter of the grinding ring is 66 inches, the rolls, three in number, weigh 950 lbs each, and are 24 inches in diameter, the pressure of each roll on the ring is about 11,200 lbs. On limestone this mill will grind from 30 to 40 tons an hour, 35 per cent. of the product passing a sieve of 200, 55 one of 100, and 98 one of 20 divisions to the lineal inch. It is represented by Fig 34. On rotary clinker the product is about 25 tons an hour.
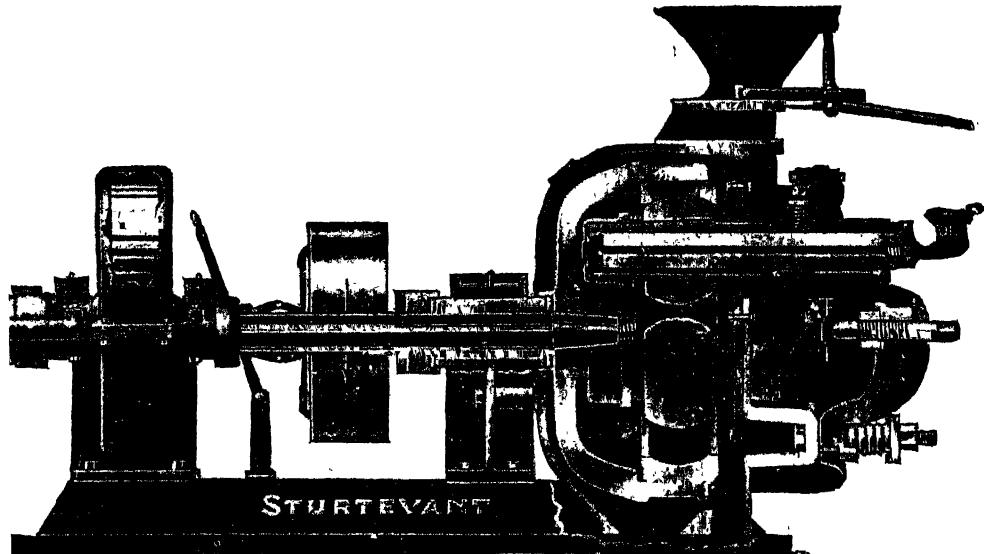


Fig. 35.—Sturtevant Ring Roll Mill—Section.

**The Sturtevant Ring Roll Mill.**—In this, a heavy steel ring is securely attached to a horizontal revolving shaft. The working face of the ring is concave, that of the rolls, three in number, convex; they are secured on long sleeves which rotate on fixed steel shafts of great strength. The material to be ground, none of which should exceed 1¼ inches in size, is delivered into the mill by an automatic feeder, it is driven against the ring by centrifugal force and is drawn under the rolls. There is no actual contact between the ring and the rolls, the face of the ring being always covered with a thick layer of material, which is crushed and ground upon itself, the rolls being caused to rotate by the action of the revolving ring. The ground product escapes from the case on each side of the ring. One adjusting screw regulates the pressure, which may be from 20,000 to 40,000 lbs., distributed equally

and elastically on all the rolls, and also allows them to be held away from the ring when the mill is running empty. By removing four bolts, the entire front of the mill, to which the rolls and all their working parts are attached, may be swung open, and the whole interior exposed. The only renewals required are the ring and rolls, their duration depending on the nature of the material ground. Fig. 35 illustrates the mill in section, Fig. 36 in front view with open door. It is made in three sizes, 24, 33, and 44 inches diameter
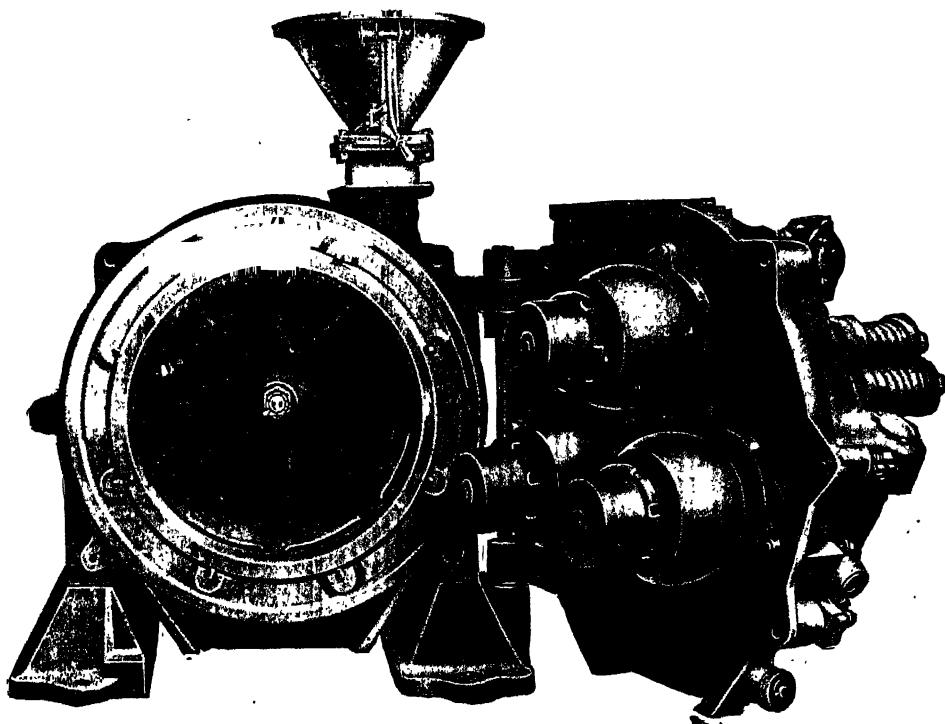
Fig. 36.—Sturtevant Ring Roll Mill—General View with Door open.

of ring. In the two smaller sizes the rolls are 14 inches in diameter by 7 inches width of face, in the larger one, 18 inches by 10 inches.

The product from the mills consists largely of material already ground sufficiently fine, which is collected in a worm conveyor, and is distributed uniformly along the upper edge of the "Newaygo Screen Separator." This piece of plant is illustrated by Fig. 37, and is shown in section by Fig. 38. On referring to the section, it will be observed that there are two screening surfaces, an upper one, which is of coarse mesh, but sufficiently fine to retain any material too large for tube mill feed. The lower one is

of fine mesh wire cloth, and is maintained in a state of high tension: it is supported on springs and kept in a state of vibration by slight hammer taps, the mechanism for which is shown in the illustration. The whole apparatus is enclosed and dustless, but the interior may be instantly exposed by raising the hinged cover above the screens.

The separator makes three products. 1. That rejected by the upper screen, from which all the sufficiently fine material and the fine grit has been
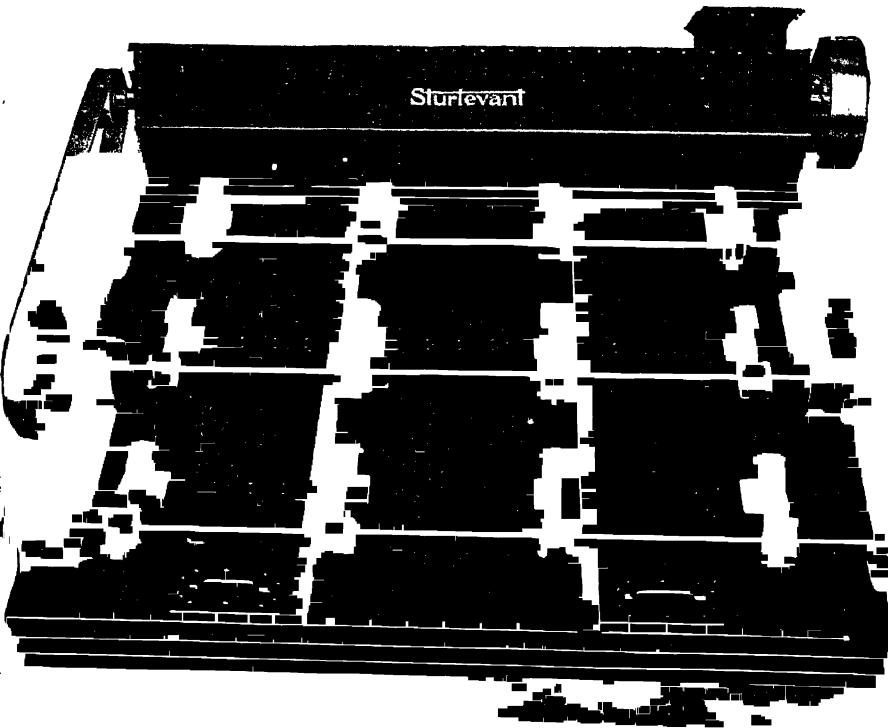


Fig. 37.—Newaygo Screen Separator.

removed. It passes automatically to the mill. 2. The grit rejected by the fine screen, which is finished in a tube mill. 3. That passing the fine or finishing screen which, together with the product from the tube-mill, is conveyed to the silos.

**The Kent Mill.**—In general design, this is somewhat similar to the Sturtevant mill, but it differs in its details. The grinding ring is not itself driven, but is free to revolve, and has a slight lateral movement. The uppermost of the three rolls is driven by a pulley and belt and turns the ring by

friction against it ; the other two rollers are driven by friction against the ring ; a thick layer of the material in course of being ground intervenes between the rolls and ring. All the rolls are fixed to their spindles, which revolve in bearings outside the grinding chamber. Pressure is applied to each roll separately by means of powerful springs and adjusting screws. The product from the mill is dealt with by an air separator, the grits being returned to the feed hopper of mill for further grinding.
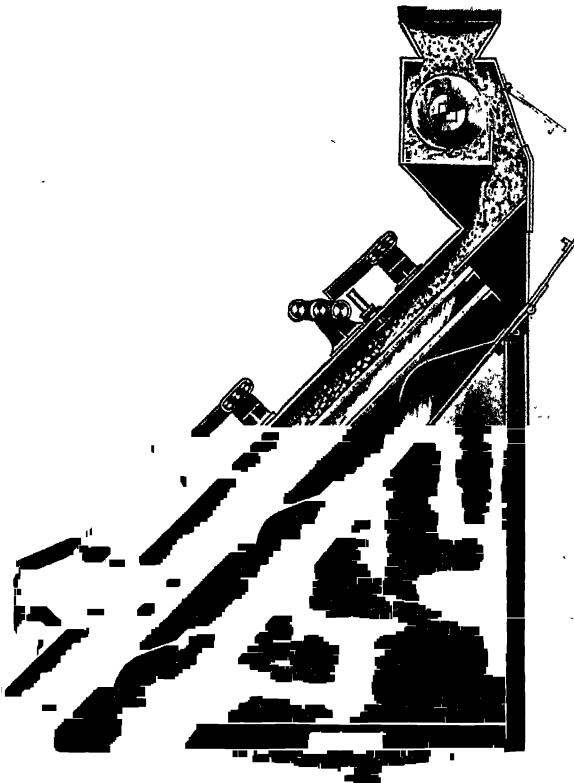


Fig. 38.—Newaygo Screen Separator—Section.

**The Sieveless Ball Mill with Air Separator.**—This consists of a drum, the stepped grinding plates of which are not perforated. They are arranged with slits through which the coarsely ground material passes into a hopper from which it is lifted by an elevator to an air separator. This removes the sufficiently fine portion, the material rejected passing directly from the

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separator to the inlet opening of the mill.   The grinding bodies are steel balls,
as in the ordinary ball-mill.   Fig. 39 shows the arrangement of the Pfeiffer
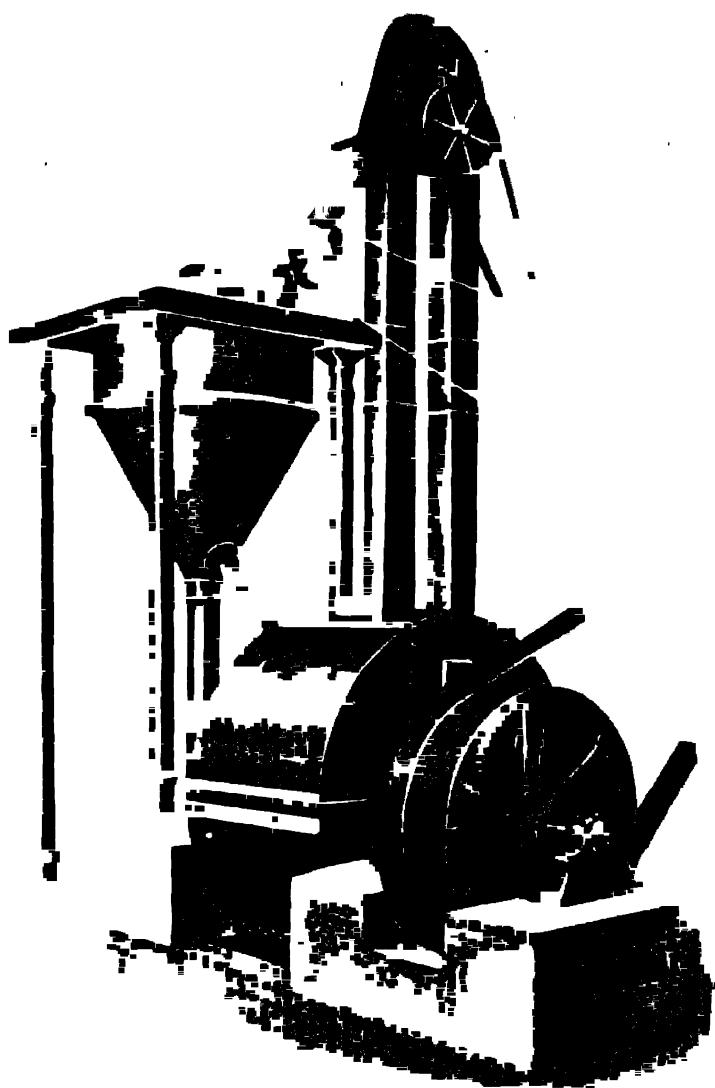
Fig. 39.—Sieveless Ball Mill, with Air Separator—General Arrangement.

mill with elevator and separator. The method of driving shown here is by gearing, the shaft passing through the mill. In a recent improvement, the ends of the drum are encircled by renewable rings, or tyres, which bear on friction rollers. These are not arranged symmetrically, one pair being at a much lower level than the other, and, consequently, bearing the major part of the weight. The driving shaft works with a pulley and belt, and is kept outside the mill, which is driven by friction between the rollers and the tyres.

The Air Separator. — About 1884, Messrs. Mumford & Moodie devised, and patented, a system by which the coarse and fine portions of a roughly ground material are separated by the action of a current of air. This system was first applied to mills for grinding phosphates, and, as introduced and manufactured by Messrs. Askham, it rapidly found its way into the cement industry. Its action will be understood by reference to Fig. 40.

A is an outer casing of sheet iron circular in form, into which the fine dust is thrown; it terminates in a spout at the bottom for delivering into casks, bags, or a conveyor, as may be desired. B is an inner casing, into which the coarse particles fall, and can be delivered to the right or left through the branch pipes, $a\,a$, by moving the valve $c$. A movable band, C, encircling the top of the case, B, acts as a damper for closing the opening between the cases A and B, and is worked by the lever $f$, and the rods $h\,h$. D is the hood, against which the material is thrown, E E blades



Fig. 40.—The Mumford & Moodie Air Separator.

of fan connected by arms to the disc $E^1$, rotating on the fan spindle $E^2$. The spindle and driving gear are carried by the standard F; G is the feed cone into which the material is inserted.

The material to be treated is fed into the cone G, and falling upon the rotating disc $E^1$ is thrown in a thin stream all round towards the fixed hood D. The current induced by the fan passes upwards, and carries with it the fine particles which are thrown into the outer case A, the current of air separating itself from the fine particles by centrifugal force returns through

the opening in the direction of the arrows, the same air being used over and over again. The coarser particles which are too heavy to be lifted by the current of air fall into the casing B, from whence they are discharged by the branch pipes, *a a*, and are returned to the mills to be further reduced. The degree of fineness of the finished material can be regulated by the speed of the fan, and by means of the damper, C, which intercepts the current of air. Different forms of hood, D, also alter the quality of the finished material.

This separator, as originally designed, has been improved in some of its details, but the general principle remains the same. It is necessary for its successful working that the material treated should contain a considerable proportion of coarse grains, from which the fine portion may be removed by the current of air. The separator will not work on fine powder alone.

**The Raymond Mill and Air Separator.**—This is a pendulum mill which may have from two to five rollers combined with an air separator. It is illustrated by Fig. 41. By the action of the air current drawn through the mill by the exhaust fan, the material, as fast as ground, is at once withdrawn into the separator above the mill. That portion sufficiently fine passes through the fan into the cyclone collector, the coarse particles fall from the separator back into the mill, which is entirely closed, the air supply being drawn from the collector through a series of openings arranged below the grinding ring. Thus, the same air constantly circulates through the whole apparatus. To prevent this from becoming heated, a little external air is admitted while the machine is in operation. The excess air escapes by a valve in the pipe connecting the collector and the mill. In the illustration it will be observed on the top of the bend. This air carries away in suspension a little fine dust, which is generally disregarded. If it is desired to remove it, or if the material being ground is a valuable one, a tubular dust collector is provided.

When an extremely fine product is required, the mill is enclosed with a vertical casing to a height above the working parts and a separator of similar form to that illustrated, but of different internal construction, is erected upon this casing. It has an inner cone between which and the outer one the ground material is drawn, the coarse particles falling back into the mill through the inner cone. An arrangement of deflectors is provided for regulating the fineness of the product. The mill is driven by bevel gearing, which is not shown in the illustration. For the reason that it operates with absolute freedom from dust, this plant is especially suitable for grinding coal, and for separating slaked lime : for these purposes it is in extensive use in the United States. It may be employed for grinding cement raw materials, but it is not suitable for clinker.
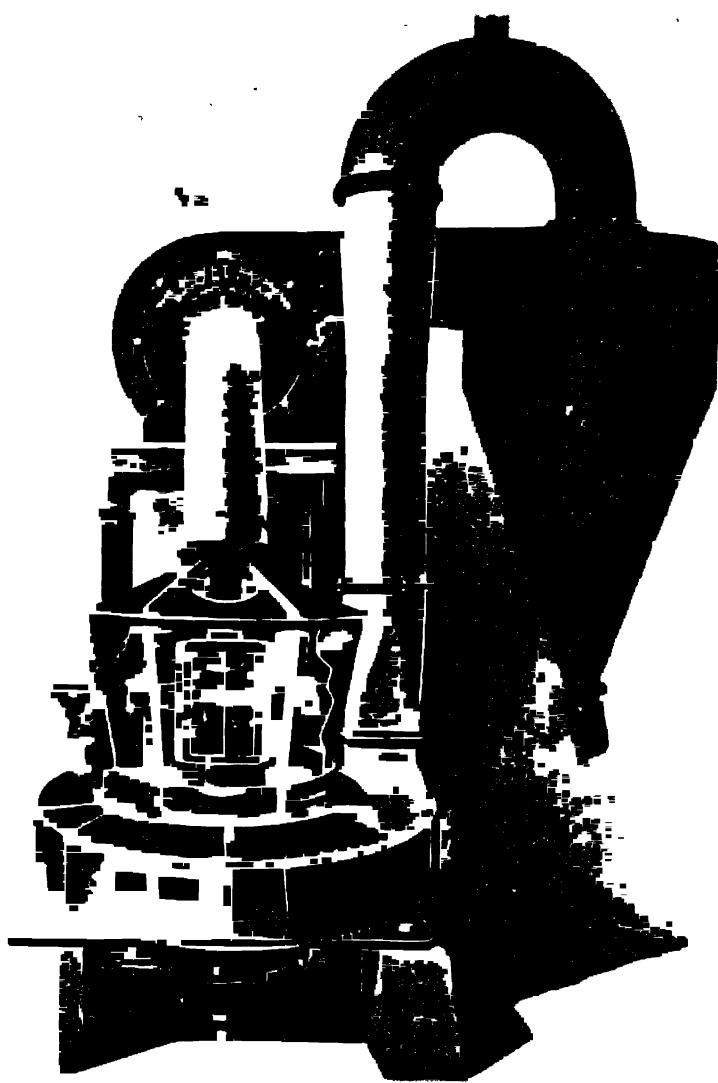
Fig. 41.—Raymond Mill and Air Separator.

## CHAPTER X.

## CONVEYORS, ELEVATORS, AND METHODS FOR COLLECTING DUST.

CONTENTS.—The Screw or Worm Conveyor—The Belt Conveyor—The Tray Conveyor
—The Marcus Conveyor—Belt and Chain Elevators—Dust-Collecting Appliances.

**Transmission of Materials.**—The automatic transmission of materials from
stage to stage during the process of manufacture of Portland cement is an
important consideration. When designing new plants every care should
be taken to minimise the use of appliances of this kind, as they are not
themselves productive, they absorb power, their upkeep is costly, and a
trifling accident to only a small section may often occasion a stoppage of
the whole plant. In the alteration, or reconstruction, of existing plants,
it is frequently necessary to employ them to a considerable extent, but
in both cases they should be well designed, and of good construction. Ex-
perience often results in increased output being obtained from existing
machinery by very simple means, and it is advisable to construct trans-
mission appliances to take a moderate overload in the case of this occurrence.
Appliances for transmitting material horizontally are known as conveyors,
those acting vertically, as elevators. A brief description follows of those
most generally employed.

**The Screw or Worm Conveyor.**—This is probably the earliest form of
conveyor. It is often found in old corn-mills, constructed of an octagonal
shaft of soft wood, into which flat blades of hard wood are inserted to produce
a worm of any required pitch. A later type was built up of cast-iron sections
of screw form, either threaded on a square shaft, turned at intervals to form
bearings, or secured by set screws on a round shaft.

It was found, as the results of experiments, that the actual work of
conveying was all done by a narrow portion of the circumference of the screw,
the remainder being of no value as regards carrying capacity, but really
occasioning loss of power by friction. This led to the introduction of the
spiral or skeleton-conveyor, formed of a strip of steel coiled in long lengths
by a special machine to form a spiral of uniform pitch, which is secured to a
shaft by steel attachments. One side of these radial attachments is flat,
and is bolted to the spiral band, the other end is formed into a split eye,
which clips the shaft and is secured by two bolts. The shaft with the con-
veyor is suspended by hangers in troughing, made either of pressed steel
or cast iron. The shafts are connected by muff couplings, split in one place

and bored to pass upon and grip the shaft when slightly opened. The ends of the shafts are grooved about ¾ inch wide and ½ inch deep, and a loose tongue is fitted in. The coupling bolts, two in number, are recessed into the shafts



Fig. 42.—Spiral Conveyor.
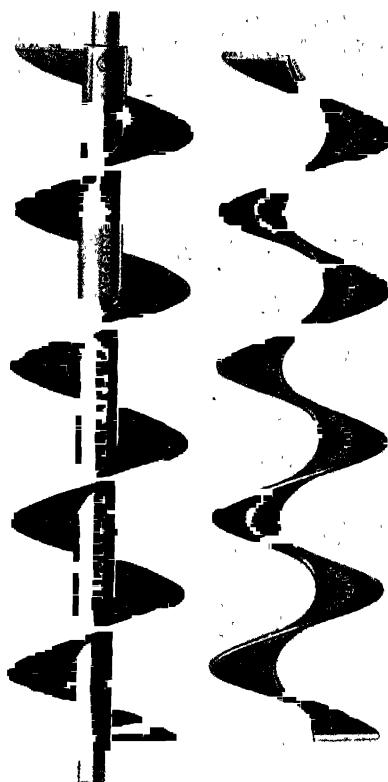
Fig. 43.—Improved Form of Spiral.

to a depth of one-half their diameter. A good form of construction is to fit in short lengths of shaft, where the bearings occur, with a coupling at each end. When worn they are easily renewed without disturbing the conveyor. This form of conveyor is illustrated by Fig. 42.

An improved form of spiral is shown by Fig. 43. The edge is thicker on the inside against the shaft than on the outside, and it forms a solid worm. It is secured to light drawn steel tubes, which it exactly fits, and which form the shaft, by fixings, flat at one end for bolting to the spiral, the other end being an ordinary bolt with nut which passes through the shaft. Short lengths of shafting in bushes secured in the ends of the tubes form both bearings and couplings. Instead of a coiled spiral, a solid worm may be built up in sections, which are cut from steel plate, and stamped to the required pitch. They are assembled on the hollow shaft, overlapping each other, are fastened together by bolts or rivets, and are secured to the shaft in the same manner as the spiral.

Both the skeleton-spiral and solid worm conveyors, although very efficient for transport purposes, do not to any great extent mix the material carried. If mixing, as well as transmission, is required, or if the material conveyed is damp, a paddle blade conveyor should be used. Fig. 44 shows
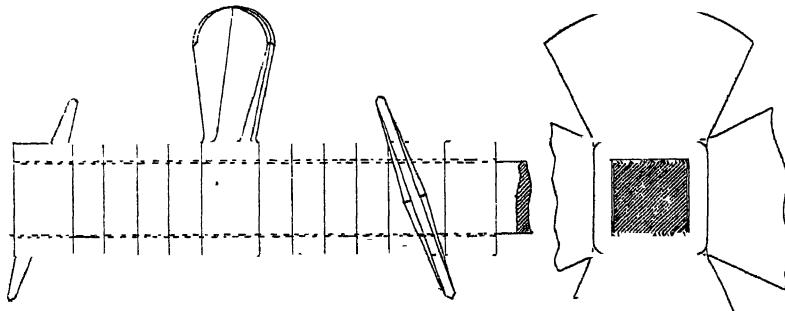


Fig. 44.—Paddle-blade Conveyor.

one type in which the blades are of chilled cast iron, and slip on to the square shaft with loose collars between them; the blades or collars at the ends, or where the bearings occur, are secured either by set screws, or, better, by bolts passing through the shaft. In this type the blades must be either right- or left-handed, according to the direction in which the conveyor or mixer is required to transmit. It is sometimes practicable to reverse the direction by altering the arrangement of the driving gear, or by crossing the driving belt. In the example shown by Fig. 45, the blades are of cast steel with shanks that pass through the shaft, and are screwed and secured by nuts. Here it is obvious that, by reversing the angle at which they are set on the shaft, the same blades may be used to carry either to the right or the left without altering the drive.

Worm conveyors are adapted for transporting fine or granulated material. The pitch of the worm should be equal to its diameter. The capacities of the spiral and paddle blade conveyors are about equal, and are about one-fourth

less than that of the solid one, all being of the same diameter, and operating under similar conditions. The speed may vary considerably, that for a 9-inch worm, a very usual size in a cement works, may be from 80 to 100 revolutions per minute.
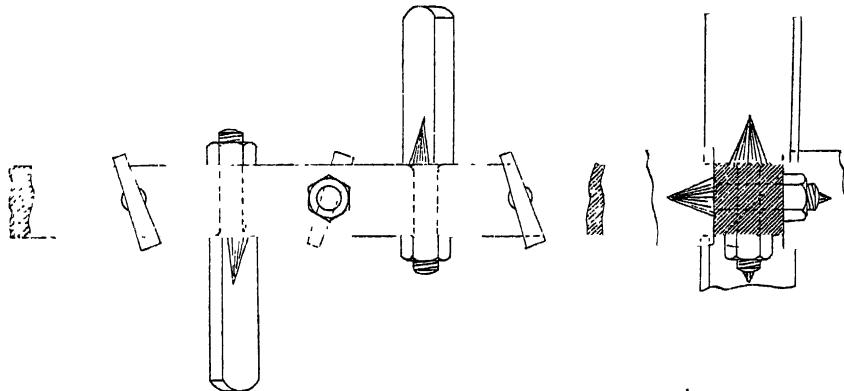


Fig. 45.—Paddle-blade Conveyor (Wedge Cutters).

**Belt Conveyors.**—An endless belt, supported by rollers, will convey almost any material, whether in a coarse or fine condition, and it will carry up an incline of from 15° to 20° from the horizontal without loss of efficiency, if due regard is paid to the nature of the material carried, and to the speed of the belt. The general construction of a belt conveyor will be understood
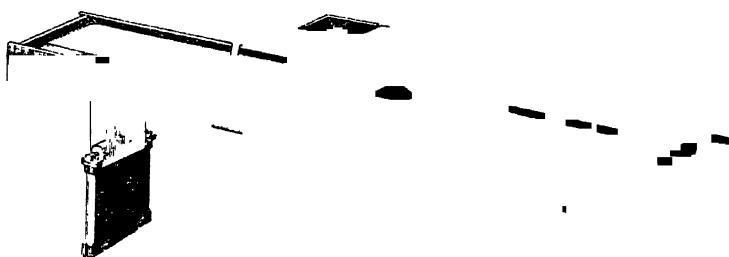


Fig. 46.—Belt Conveyor.

from the illustration, Fig. 46. The belt may be of solid woven cotton, or may be built up of cotton canvas, and balata, or rubber. The end fittings are those in ordinary use for power transmission, but the pulley at the delivery end should be provided with tension gear for taking up slack as the belt stretches, unless a travelling throw-off carriage is used, or the belt is a very

long one.  In these cases, tension is obtained by a jockey pulley loaded with weights, which rides in a loop of the belt.  The rollers for carrying the belt are from 4 to 6 inches in diameter, their spacing depends upon the nature and size of the material carried.  For light materials, such as cement and raw flour, they may be spaced on the carrying side 5 feet apart, for clinker or broken stone, 4 feet.    On the return side, the spacing may be twice these distances, one return to every two carrying rollers.  A trough-like form is sometimes given to the carrying side of the belt.  This is effected by an arrangement of side rollers, which turn up the edge of the belt, and are set at the necessary angle to produce the amount of curvature required.  These rollers also serve to keep the belt in position, and, for this purpose, it is generally necessary to place vertical rollers at intervals, when using flat belts. If required for conveying from point to point, the load may obviously be thrown off at the end of the conveyor; it is, however, generally required at some intermediate place, or at many places.  When this is the case a travelling throw-off carriage, which is shown by the illustration, may be used.  The upper roller lifts the belt to allow its load to fall into the hopper from which it is distributed on both sides of the belt, returning to its normal position by passing underneath the lower roller.  The carriage, illustrated, is of quite simple construction, and can be put out of use by removing the rollers.  In another form of carriage, arrangements are provided for swinging it into such a position as to enable the belt to travel in its normal course. If the use of the carriage is discontinued, the consequent slack in the belt is taken up by the loop and jockey pulley previously mentioned.  This is shown in the illustration near the extreme end of the conveyor, but it may be placed in any other convenient position.

With a flat belt, ploughs hinged to the framing to lower upon the belt may be used to sweep off the charge.  They may be V-shaped to throw off equally on both sides, or set at an angle to deliver on either side, in which case a straight flat bar may be bolted to either side of the V.  They should be placed in close proximity to a roller, to avoid the sag of the belt.  This arrangement is a very convenient one for supplying hoppers feeding a row of mills.  In some cases, a travelling plough running on the framing will be found convenient.

For cement factory work generally, a belt speed of 250 feet per minute will be found satisfactory.  The material conveyed should be fed upon the belt at the same speed at which it is travelling, and in the same direction.

**The Tray and the Swinging Conveyor.**— Fig. 47 illustrates the tray conveyor.  It is formed by short trays which overlap each other, and are secured to an endless chain passing over sprocket wheels, one of which is provided with gear for taking up slack caused by the wear of the chain.  It is a good conveyor, but has the disadvantage that delivery at intermediate points is impossible.

The swinging conveyor consists of an open trough to which, at intervals,. spring legs are attached.  These may either be secured to a floor, or, if more convenient, to a suitable construction overhead.  The trough is made of very light steel plate, as, contrary to what might be expected, it is subject to but little wear.  By means of a small countershaft and crank, and the action of the spring legs, a forward and slightly rising motion is imparted to the material in the trough, which is rapidly carried to the point of delivery. It may be of any reasonable length (an instance has been given of one 300 feet ·long), it may be driven at any point in its length, and it can be lengthened without interfering with the driving mechanism.  The conveyor may be fed at any desired point, and the material can be drawn off wherever required, by means of openings fitted with slides.  It will carry on an upward gradient
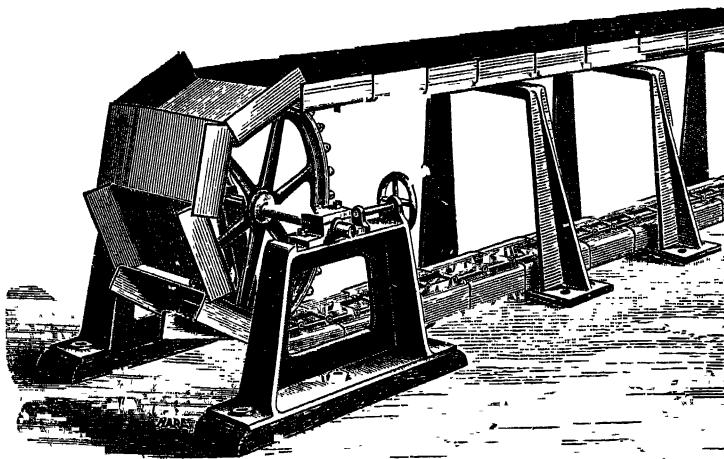


Fig. 47.—The Tray Conveyor.

of 1 in 20, and it is claimed that it will convey any material, fine or coarse,. either in a dry or in a damp condition.  The power required for delivery is small, a conveyor driven by a belt 2 inches wide will convey 7 tons per hour.  Our own knowledge of it is confined to its use for transporting broken stone, for which purpose it proved to be admirably adapted.

**The Marcus Conveyor.**—This is shown by Fig. 48.  It consists of a trough,. made of light steel plate in three forms, adapted to the material to be conveyed.  On the under side, it is provided with carriages having flanged rollers, which are placed at intervals and rest on steel channels or light rails.  By means of special driving mechanism of simple design, which is fixed on a separate foundation, a backward and forward motion of about 12 inches is given to the trough, causing the material it contains to be

rapidly carried along. This conveyor has been largely used for transporting the clinker from rotary kilns. The makers, Messrs. Head, Wrightson & Co., give an example of one extending for a length of 328 feet in front of the coolers from a row of these kilns. The trough is $19\frac{3}{4}$ inches wide at top by 13 inches at bottom, with sloping sides. Its hourly capacity is from 30 to 40 tons, with a consumption of from 5 to 6 H.P.



Fig. 48.—Marcus Conveyor.

**Elevators.**—These consist of endless belts or chains, travelling either over pulleys, or alternatively over sprocket wheels, to which are attached at regular intervals buckets, which lift and deliver the material to be elevated. The buckets are stamped from steel plate, without seams or overlapping edges, and with round corners to facilitate delivery, and they may be obtained in a great variety of patterns, capacities, and thickness of plate. Belt elevators are not suitable for dealing with coarse, heavy materials, but in some cases they may be used for elevating powders. Chain belts, however, are generally preferable.

Detachable link chains of cast steel or of malleable cast iron, with suitable links, to which the buckets can be attached, may be obtained in many forms and sizes, Figs. 49 to 53 give examples of elevator details. Fig. 54 shows the head of an elevator with sprocket wheel, by which the chain is carried round. A similar wheel is provided at the bottom. Fig. 55 shows a complete vertical elevator without the casing. The upper wheel is of larger diameter than the lower one, for the purpose of obtaining a clean delivery. Fig. 56 shows an inclined elevator fully cased in. It will be observed that tension gear is provided in the bottom fixing, or boot, for taking up slack

caused by the wear of the chain, and also hand holes for obtaining access for cleaning out when necessary. On inclined elevators, bars of flat iron projecting on each side of the buckets should be placed between them and the attachment links. These run on both the up and down journey on bars fixed to the framing, which serve to prevent sagging of the chain.

**Dust-Collecting Appliances.**—In whatever manner the Portland cement materials may be mechanically treated, it is impossible to prevent the formation, at certain stages of the process, of considerable volumes of dust, and this



Fig. 49.—Detail
of Belt Elevator.
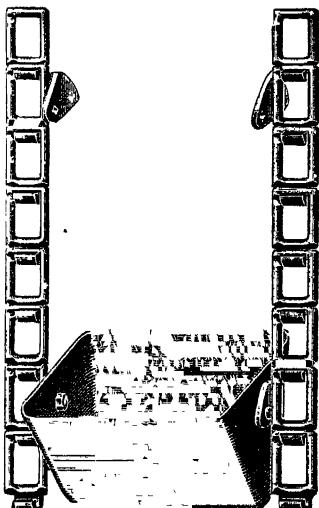
Fig. 50.—Details of Chain Belt
and Elevator.

dust may not only become a source of annoyance, and injury to the health of the workmen, but it may also entail a serious loss to the manufacturer, if precautions are not taken to keep it under control and to collect it by means of suitable contrivances. With the wet process, dust is only produced by the cement grinding side of the plant, but, with the dry process, that from the raw grinding side has to be considered in addition, and this is about one and a-half times as much as that from the cement. The fact that the wet process produces a smaller quantity of dust than the dry has been used
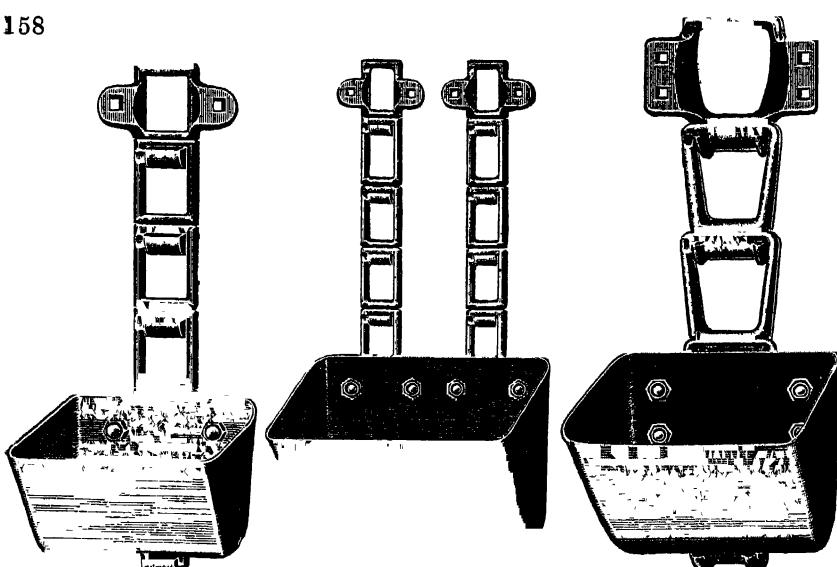
Figs. 51, 52, 53.—Details of Chain Belt and Elevators.
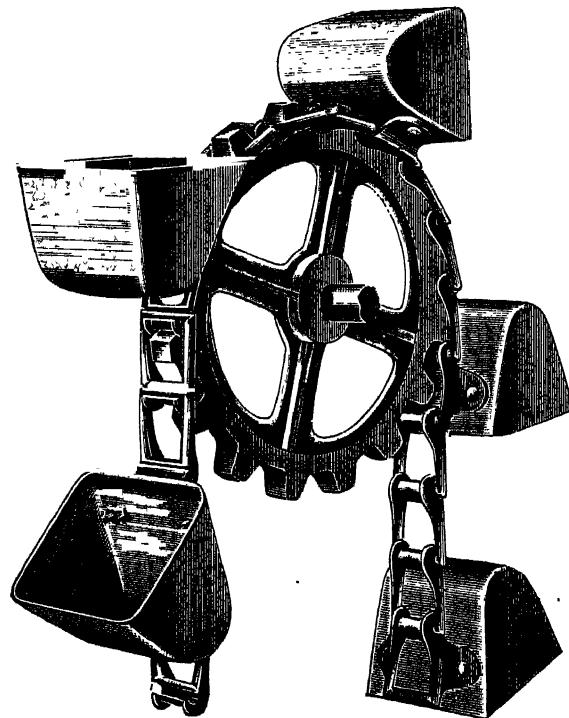


Fig. 54.—Detail showing Head of Elevator.
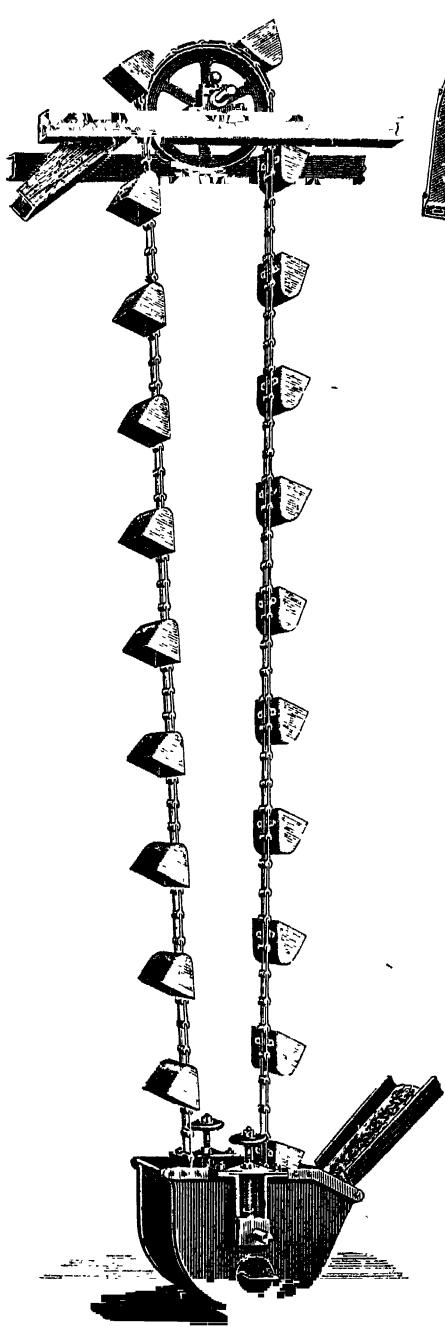
Fig. 55.—Vertical Chain Belt Elevator.
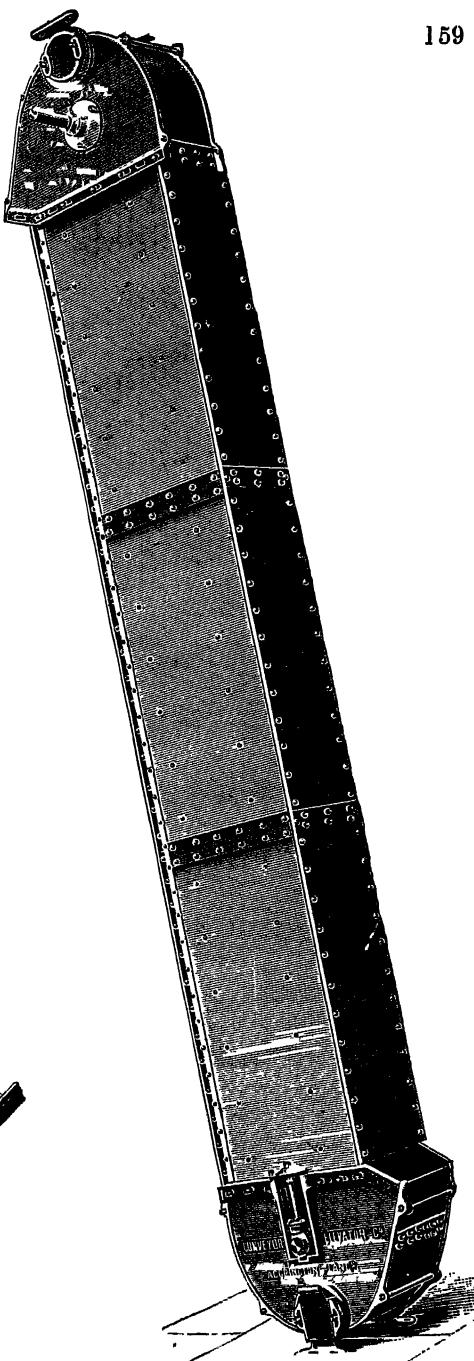
Fig. 56.—Inclined Elevator, with Casing.

as an argument in its favour. The separation of the dust suspended in the cases from rotary kilns will be considered when we deal with these kilns.

To obtain successful results, the dust should be carried away, at the point at which it is generated, by means of accurately proportioned piping, connected with suitably designed collecting hoods, or preferably directly with the machines or appliances from which it is evolved. These pipes are connected with a main trunk, through which the dust-laden air is drawn by means of an exhaust fan. In order to separate dust from the atmospheric air in which it is suspended, there are three systems available which are capable of giving good results :- (1) By the employment of filtering apparatus ; (2) by the aid of centrifugal action ; and (3) by bringing the air to rest in suitable chambers.

The first of these systems, if properly carried out, frees the air almost entirely from all the particles suspended therein. Air-filters usually consist of a number of sheets of cloth or flannel fixed in light frames, through which the air is caused to pass by an induced draught. It has been found advantageous in cement works to employ a special apparatus for filtering purposes, in which the frames can from time to time, by means of taps and blows, be freed from the dust which has collected on the surface of the vertically-arranged cloths, and in which the cloth can be cleansed by reversing periodically the current of air, so as to blow out the dust from the pores. A filter of this kind has been produced by Messrs. Nagel & Kemp, and their apparatus provides a large filtering surface by arranging the frames in a cylindrical chamber, so as to radiate round a central inlet ; the dusty air passes in at the bottom, and the purified air is drawn out at the top by means of a fan. In another kind of filter, the patentee makes use of a series of lengths of hose enclosed in a chamber ; the dust-laden air passes up through the hoses and parts with the dust, which adheres to the inner surface of the hose. The portions of hose are from time to time freed from the dust by being beaten or shaken, and the pores are cleansed by reversing for a short time the direction of the air current. These hoses are arranged in pairs in air-tight receptacles, and the battery may consist of any number of pairs from one to twelve, the total height being 13 feet, and the diameter of the fans needed to work them ranging from 12 inches to 60 inches. The dust falls to the bottom of the chamber, and may either be removed continuously by a screw-conveyor, or it may be from time to time withdrawn when the hoses are being cleaned. Filters of this kind are largely used on the Continent in factories where much dust is produced.

In some cases the filter itself is made to revolve, and by this means a large filtering surface is obtained in a comparatively small space. The filter cloth is star-shaped and is fixed on a rotating drum, so that separate cells are formed which are cleaned automatically by tapping. As the entire apparatus is contained within an air-tight cylindrical casing of wood or

iron, it is entirely dust-proof, and it can be made to work with its own fan or with any suitable draught producer.

A filtering apparatus of a somewhat different type consists of a horizontal tube, the lower half of which is constructed of sheet iron, and the upper part of flannel or woollen cloth. The dust-laden air is passed into this tube, in which is fixed a revolving shaft furnished with spiral brushes. These brushes serve to carry the dust to the end of the tube, whence it is removed by a screw-conveyor, while at the same time they free the woollen surface from dust and facilitate the exit of the purified air.

The centrifugal system of dust-collecting is much less perfect than any of those we have already described. The dusty air is admitted—in one form of machine, the " cyclone "—to an upper cylinder constructed of metal in a powerful current caused by a fan or blower. The current enters tangentially, and the dust follows the windings of a spiral until it reaches the outlet, and falls into a conical receptacle placed below the cylinder, while the air, freed from dust, escapes by an orifice in the top of the cylinder, and is usually permitted to pass up a pipe to the exterior of the building.

Under the third method of dealing with dust, the settling chambers are usually of large size, and they are arranged to occupy some vacant area in the roofs or in the upper part of the factory. These chambers may conveniently be divided into cells by a series of hanging screens or frames, covered with canvas, and for readily collecting the dust the floors are often hopper-shaped, so that the particles fall to the bottom and admit of easy removal.

Theoretically, the action of such chambers depends upon the possibility of bringing the air into complete rest, and the extent to which this can be done is founded upon the relative size of the chamber as compared with the volume of the dust-laden air which has to pass through it. Even under the best conditions, this plan of freeing the air from impurities is far from perfect, but very considerable quantities of dust can be intercepted by this means, and the annual value of the cement which is obtained in this way will pay a good interest on the initial cost of constructing such chambers.

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CHAPTER XI.

## PREPARATION OF THE MIXTURE OF PORTLAND CEMENT RAW MATERIALS BY WET METHODS.

CONTENTS.—Uniform Mixture Essential—Preparation of Thin Slurry—The Washmill—Backs—Drying Floors—Goreham's Process—Slurry from Hard Materials—Description of Slurry Plants—Regulating the Composition of Slurry—Use of Marl in America.

**Uniform Mixture Essential.**—It is not only necessary that the correct proportion of carbonate of lime to clay substance should be maintained, but the mixture must also be uniform, and its constituents must be in an extremely fine state of subdivision. This is attained in practice by one of two methods : —(1) By the wet process, the correct quantities of the ingredients being ground in the presence of more or less water ; or (2) by the dry process, by which the perfectly dry materials are ground together, although in some cases they are roughly ground separately, the coarse powders being subsequently mixed in the required proportions, and afterwards finely ground. In certain circumstances when employing the wet process the materials may with advantage be ground separately.

**Preparation of Slurry.**—The methods employed for preparing the slip or slurry of the wet process will now be described ; those for the preparation of the raw flour or meal made use of under the dry process will be dealt with in the chapter following.

It is interesting to note here that Aspdin, the original inventor, insists upon grinding the ingredients to a " state approaching impalpability," and this is as true now as it was in his day. Probably more failures with the use of cement have been due to neglect of this precaution than to any other cause, even including the employment of incorrect proportions of the constituents. An imperfect coarsely ground mixture when once it has reached the kiln is, to a great extent, past redemption. If it is known to be faulty it may to some extent be corrected by very hard burning—that is, if the mixture is so proportioned as to admit of this treatment. Some improvement may be effected by watering and storing the clinker before grinding, and by grinding it to an extreme degree of fineness, but the resulting cement can never possess the properties of that made from carefully-prepared

clay are introduced into the mill, either continuously or from time to time
at stated intervals, together with such a supply of water as to keep the
contents constantly at the overflow level.   By the action of the knives
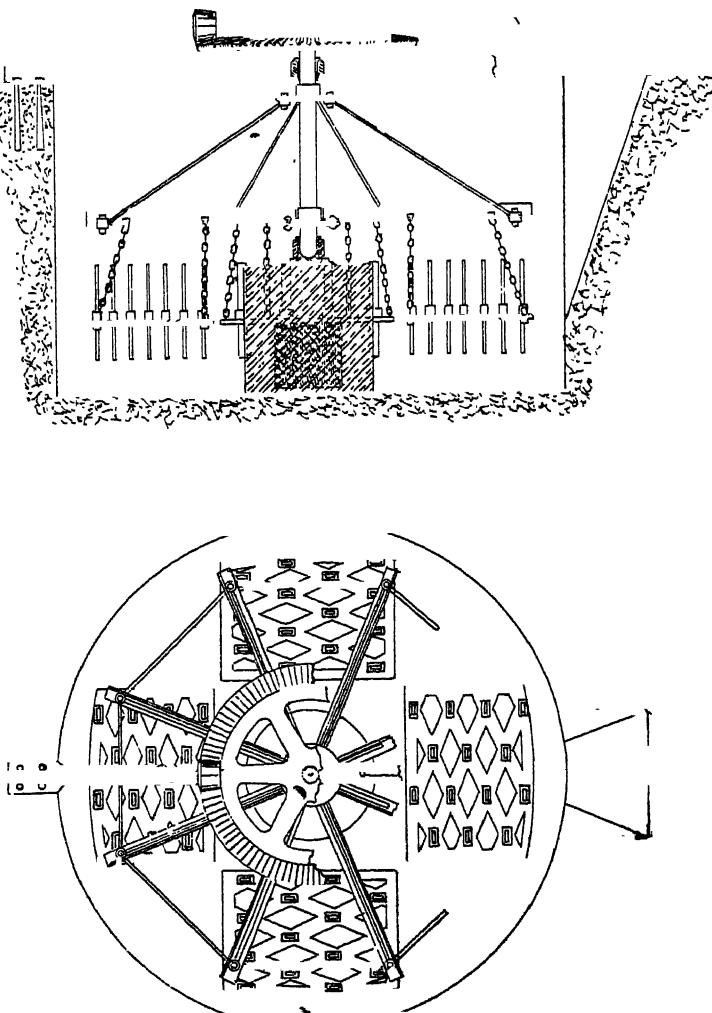


Fig. 57.—Washmill—Section and Plan.

attached to the revolving beam the contents of the raceway are violently
agitated, the clay is broken up, while the lumps of chalk are comminuted
by attrition and reduced to a state of fine division.   These substances are

also evenly distributed throughout the water, the result being a creamy liquid termed the " slurry," which is driven through the meshes of the sieve by the scour, and is led away by troughs to the depositing backs.

In the modern type of mill, harrows are substituted for the beam with knives. These are formed of cast iron, they are fitted with steel tines or teeth, and are suspended by chains from radial arms which are attached and braced to the vertical shaft, and to each other. The suspended harrows adapt themselves better to the deposit of stones and flints which collects in the bottom of the raceway than does the rigid beam in the older form of mill.

In some cases harrows have been replaced by heavy edge runners for dealing with hard chalk free from flints, and mills of this type have given good results. For soft chalk they are unnecessary, as harrows will do the work quite as efficiently, while for chalk with flints edge-runners are obviously unsuitable. Our own experience goes to show that fairly hard chalk, such as occasionally occurs in the South of England, may be very effectually triturated in a mill fitted with harrows, if it is broken reasonably small, or preferably passed through toothed rollers, and the feed is uniform and not excessive. This statement, however, does not apply to indurated chalk, such as that of Yorkshire or that of the North of Ireland. The mill may be constructed of concrete, or of brickwork, built in cement mortar, the facing being of very hard bricks. The raceway should be paved with hard material, such as granite setts, and these also should be set in cement mortar.

The question as to whether the materials should be weighed, or be measured, into the washmill has often been debated. If they were invariably in the dry condition, or their content of water was always uniform, there could be no question as to which plan would give the most accurate results, but in their normal condition they contain more or less water, and they are also very absorbent; the quantity of water present consequently varies in accordance with the state of the weather. If equal quantities of each material were used, and if each was equally absorbent, it is evident that weighed quantities might be employed in all conditions of weather; but the quantity of chalk being in round numbers three times that of the mud or clay, any proportions adjusted for use in dry weather would, if used during or after much rain, result in an abnormal mixture. Since, however, the materials do not alter in volume by absorption of water, measured quantities will practically always contain the same amount of solid matter, and may, therefore, be used with safety in both wet and dry weather.

In some cases washmills are constructed of much larger dimensions than those we have given, the waggons of chalk and clay being weighed as they are brought alongside and tipped directly into the mill. One load of clay should be tipped in at the same time as its equivalent of chalk. A reserve of each material should be kept in hand, so that the work may go on continuously

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and regularly, the mill never becoming overloaded. Irregularity of composition in the product from the washmill is in modern practice corrected by means which will be described later in this chapter, but, at the same time, care should be taken at this stage to make the mixture as accurate as possible. The sieves or screens through which the slurry leaves the mill should be kept constantly under observation, and should at once be replaced if found to be torn or damaged. The raceway from time to time requires cleaning out, especially when the upper chalk with flints is used. This precaution should not be neglected, for otherwise, as soon as the harrows begin to drag and tilt about on the uneven accumulation which gradually forms in the bottom of the mill, the efficiency of the operation is much impaired.

**Backs.**—The backs are frequently of large size, being sometimes as much as 100 feet in length by 40 feet in width, with a depth of about 4 feet. A back of these dimensions would thus contain 16,000 cubic feet or 160,000 gallons of slurry. The sides are generally constructed of brick or concrete, and the bottom is carefully formed of porous materials, so as to permit of the ready soaking away of the water. It is, of course, imperative that special attention should be paid to the subsoil drainage.

**Distribution of Slurry.**—The stream of liquid slurry, on leaving the washmill, flows into a channel, which delivers it to wooden troughing carried round the backs. The troughs are provided at suitable intervals with apertures, from which, by means of slides, the slurry may be made to enter any particular back at different places. By changing the places of admission every day, it thus becomes possible to obtain a much more even distribution of the slurry, and this is an important matter, as from the nature of the means employed to produce it, the slurry, as it leaves the mill, may not be always of normal composition. Thus at some moments the chalk may be in excess, at others the clay, though the average over a considerable period of time may be about right. By the occasional use of a drag formed of a piece of plank attached to the centre of a long rope, which is pulled about by two men, the various washings are " luted " or mixed together, and a sufficiently uniform result is obtained. Catch-pits or depressions are provided in the channel leading from the washmills, and into these any unground particles of chalk or coarse sand subside from the slowly-flowing stream of slurry. The coarse sludge deposited in the pits should be from time to time removed with a scoop.

**Subsidence of Slurry in the Backs.**—The suspended chalk and clay, when they come to rest in the back, rapidly subside ; part of the water soaks into the ground or evaporates, but a considerable quantity of the clear supernatant liquid is drawn off by means of the " peg-board," which is a perforated penstock having numerous small openings closed by pegs, the holes being arranged at such levels that the water can be run off gradually

as far as the top of the slurry.  Some weeks must elapse, even in the summer time, before the contents of a back become sufficiently consolidated to admit of removal by being dug out.

It was frequently asserted that slurry settled irregularly in the backs, the chalk and clay having, it was alleged, a tendency to separate owing to the difference of their specific gravities.  If the slurry is finely washed there is no such separation, but if coarsely washed, and if no provision is made for taking out the larger particles of chalk by catch-pits, or if due attention is not paid to cleaning the pits out, these coarse particles have a tendency to settle, and will accumulate in the lower layers of the contents of the backs.

In order to decide whether separation really took place in the case of carefully washed slurry, the following experiment was made many years ago by one of the authors.  A water-tight wooden trunk, 8 feet high and 6 inches square, was prepared, and fixed in a vertical position, where it was free from vibration and safe from disturbance.  This receptacle was filled with slurry from one of the shoots entering the backs.  The slurry had been prepared from grey chalk and gault clay, and when tested by washing through a sieve having 120 meshes to the lineal inch it left less than 5 per cent. of very fine grit, calculated on the dry slurry, which contained 75·5 per cent. of carbonate of lime.  The supernatant water was drawn off every few days by means of gimlet holes bored in one side of the wooden trunk. When the column of slurry had settled into a stiff mass, in which it was evident that no further deposition would occur, the trunk was carefully conveyed into a warm place, and fixed in a vertical position until the contents were dry.  The wooden sides were then removed, and the column of dry material was sawn into a series of short lengths, in each of which the carbonate of lime was accurately determined, with the result that there was practically no difference in the composition of any of the layers from the top to the bottom.

**Drying Slurry.**—The original method of drying slurry was on heated floors, and, although this process has long been a thing of the past, it should be briefly noticed, as it will be necessary to refer to it later.  When it became sufficiently dry to admit of this treatment, the slurry was dug in a plastic state from the backs, and was removed to the drying floors, either in deep-sided barrows or in small tipping waggons.  The drying floors were heated by passing under them the waste burning gases from coke ovens; these gases were conveyed in flues, which, on the top of the ovens and for about 10 feet beyond them, were covered by fireclay slabs.  Beyond this distance the covering was preferably formed of cast-iron plates, diminishing in the thickness from about 1½ inches at the commencement, where they join the fireclay slabs, to about ¾ inch at the further end, where the flues joined the main or gathering flue into the chimney.  This latter flue was provided

with a damper, in order to regulate the draught. The floor was made of sufficient length to utilise all the heat from the ovens, the object in providing the ovens not being to make coke, which, as a rule, could be more cheaply purchased, but to dry the requisite charge of slurry for the kilns. The front of the floor immediately over the ovens was covered to a greater depth with the slurry than the back, and the thickness of the material was so regulated that the floor could be stripped and recovered every day. The ovens were likewise drawn and re-charged every day, and with careful working a weight of coke equal to about half that of the coal employed was obtained. The coke thus produced, supplemented by gas coke, was used in the kilns for burning the slurry into clinker. This system of drying gave place to methods of utilising the waste gases from the burning kilns, in order to dry sufficient slurry for the succeeding charge. Even when this is not possible, as, for instance, in kilns of the continuous type, methods are now available which are much more economical than that above described.

**Goreham's Process.**—The system of washing the ingredients to a very liquid slip has been practically superseded in this country by the process of wet grinding with a minimum of water, which was patented by W. Goreham in 1870, but which has been used in France, at Meudon in the neighbourhood of Paris, for more than 100 years, in the preparation of hydraulic lime from a mixture of chalk and clay. The original inventor of this milling process is said by Henry Reid to have been M. Dupont, and the French works are still being carried on very much on the old lines.

Under the Goreham system, the fine sieves on the washmill are replaced by grids, the bars of which are spaced ⅜ inch apart, or, in some cases, perforated plates are employed. The chalk and clay are fed into the washmill exactly as in the case of the older method, but only sufficient water is used to produce a thick slurry, which, in the best practice, contains not more than from 40 to 50 per cent. of water. From the washmill the coarsely-ground slurry is lifted by a scoop wheel or a bucket elevator to the grinding mills. The grinding was, and still is to some extent, by French burr mill-stones, but driven at about half the speed of those for dry grinding. Emery millstones have been used for slurry grinding in the North of England, and have been found to give much better results than those formed of French burr. Tube-mills are now generally replacing millstones for grinding slurry. Originally the slurry flowed from the mills direct to the drying floors, but with the introduction of the system of drying by the waste gases from the kilns, which required delivery at a higher level, the practice became general of collecting the slurry in a tank or well, from which by means of specially designed and powerful pumps it was lifted and delivered through pipes to any required point.

This process leads to a great economy of time, and involves much saving

of space, as the backs are entirely dispensed with, while the cost of grinding and pumping the slurry is much less than that of emptying the backs. The saving of cost was, however, not great, so long as the drying was effected on floors heated by coke ovens, since more water had to be evaporated from the pumped slurry than in that taken from backs, especially when it was possible to allow the slurry to remain a sufficient time in the backs to become thoroughly stiff. Trouble was also frequently caused by the liquid slurry running through the joints of the floor into the flues and ovens.

**Margetts' Process.**—The above described method of preparing thick slurry is now general in English practice, but two methods by which it may be produced entirely by the washmill without subsequent grinding may be referred to. The first of these entails the use of the sieve devised by W. G. Margetts, which is especially suitable when soft, easily triturated chalk free from flints is employed. The slurry is mixed in the washmill with the minimum of water, the overflow being arranged to take place through perforated plates having holes through them about ⅜ inch in diameter, The feed of the ground mixture to the apparatus is in a continuous stream, and it enters the bottom of a sieve, shaped like an inverted pyramid, revolving at a speed of about 150 revolutions per minute; the sieve employed has from 20 to 30 meshes per lineal inch. During its passage up the sides the finer portions of the slurry pass through the meshes, and flow away to the pumps; the coarse particles, on reaching the top, are ejected into an outer casing, and are thence returned to the washmill. For chalk with flints the method is obviously unsuitable, as even small fragments of flint would rapidly destroy the sieves. With respect to the efficiency of this process, it may be mentioned that the manufactory in which it was employed was one of the first in this country to guarantee its cement to stand accelerated tests, which can only be obtained with certainty when a very carefully prepared mixture of raw materials is produced. The inventor, in a letter to *The Engineer*, on May 22, 1891, stated that his practice was to submit the test briquettes to the action of boiling water instead of to a temperature of 180° F., as was at that time prescribed.

**Michele Washmill.**—M. V. D. De Michele patented, in 1877, an improvement in the washmill which enabled further grinding to be dispensed with. The minimum quantity of water is still employed, but the slurry instead of flowing out at one place in the circumference of the mill, overflows through metallic surfaces which entirely surround the outer wall. The lower surface plate, forming the rim of the mill, is fixed; the upper one revolves with the stirring apparatus of the mill. A section of the mill is shown in Fig. 58. It will be understood that the grinding surfaces are provided with a certain amount of lead, or swallow. To enter the grinding rings at all, the materials must previously have undergone a considerable reduction in the mill, and, before reaching the flat or grinding surfaces, coarse particles which

may have entered are further reduced in the gradually contracting swallow.
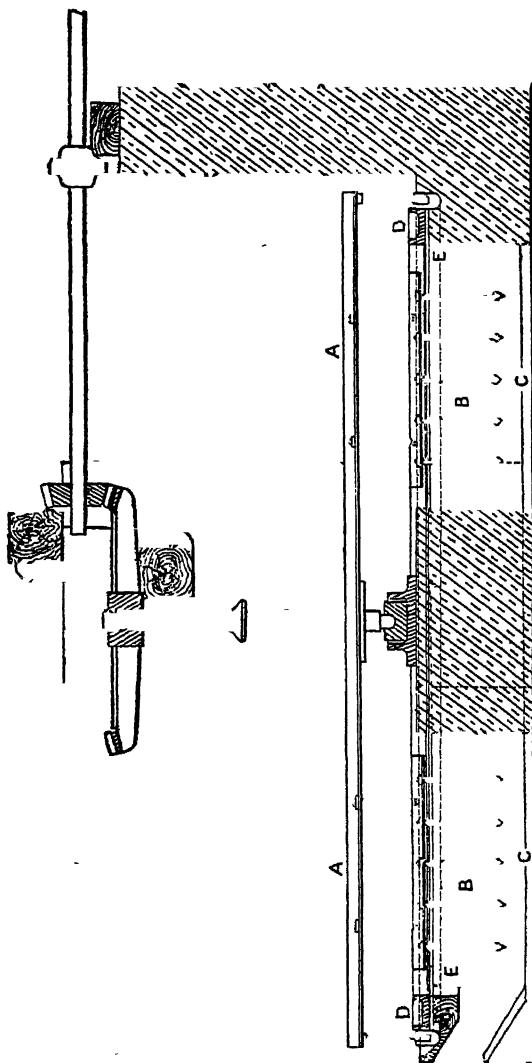


Fig. 58.—Michele Washmill.

**Slurry from Hard Materials.**—Hard raw materials for calcination in rotary kilns are sometimes prepared in the condition of thick slurry, and obviously require a different method of treatment than that previously described. Generally, the method adopted with hard limestones is to crush

them by stonebreakers, then roughly grind with the required quantity of water, finally finishing the coarse slurry in tube-mills. Steel ball tube-mills may be used for the first grinding, but better results are obtained from the Kominor, which may be adapted for this purpose.

With this plan, Messrs. F. L. Smidth & Co. interpose an arrangement called a " Trix " between the two mills. It is illustrated by Fig. 59. The
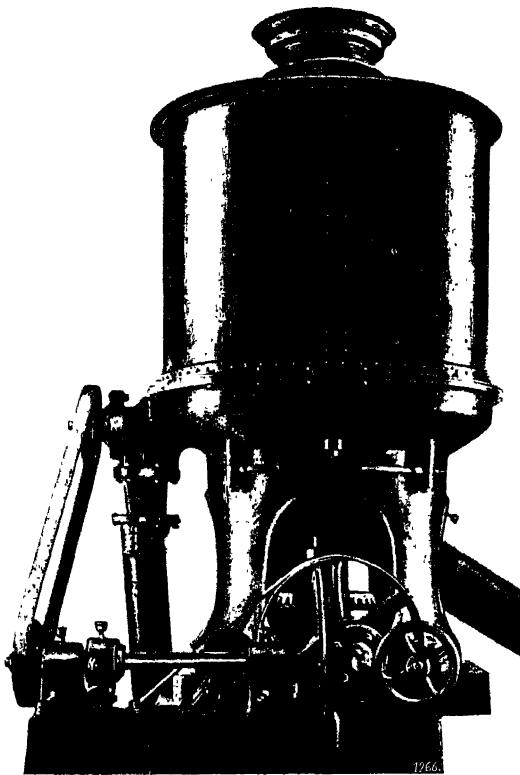


*F. L. Smidth & Co.*

Fig. 59.—Trix Slurry Separator.

stream of slurry from the Kominor enters at the top and falls into two revolving arms, which, by centrifugal action, throw it against the circular sieve. The portion passing the sieve flows by one outlet to the tube-mill for finishing, that rejected is returned to the Kominor by another outlet for further reduction.

The Fineness of Slurry.—A perfectly safe rule for the fineness of slurry is to prepare it so fine that when properly calcined the resulting cement should, as soon as ground, be capable of conforming with the usually accepted accelerated tests for soundness or constancy of volume, assuming, of course, that the chemical composition is accurate. Nothing is saved by coarse or careless preparation, which indeed is unprofitable. More fuel is required to obtain proper clinkering, the clinker produced is unnecessarily hard and difficult to grind, while the resulting cement will be more or less unsound. Although unsoundness may to some extent be corrected by grinding the cement extremely fine, and storing it before use, the additional cost of grinding the hard clinker will far exceed that of properly grinding the slurry. The fineness of slurry may be determined, as follows :—

In a portion of the sample the water is determined in the usual manner by evaporation to dryness, and heating the residue at a temperature from 100° to 105°. The water, which should be kept as low as possible, should be about from 35 to 40 per cent., according to the nature of the materials. Another weighed portion of the sample is washed through a small sieve made of thin sheet copper covered with brass gauze of from 100 to 150 divisions per lineal inch. The sieve with residue is dried at from 100° to 105°, and weighed. The weight of solid matter in the quantity taken is calculated from the result of the water determination ; from the weight of this and that of the residue on the sieve the percentage of residue in the dry slurry is · calculated. Experience will show what per cent. of residue on the sieve used, which should not be coarser than 100-mesh, is permissible. A finer mesh is preferable, but the gauze is very delicate in these and is easily damaged, and it is not easy to get the slurry through it. Using a chemical balance, we have found a sieve 2½ inches in diameter by 2 inches deep, covered with 120-mesh gauze, answer quite well, by transferring the slurry to it in small quantities and using plenty of water.

Method of Regulating the Composition of Slurry.—It will have been observed that the wet milling process as previously described is a continuous one, the stream of slurry flowing without rest from the washmills and from thence to the pumps. Some little bulking would take place in the tank supplying the mills, and in the pump well, but no attempt was originally made to check the composition of the slurry either before or after the wet milling, as it was assumed that the stream flowing from the washmill was sufficiently accurate. It was customary to sample the slurry from the backs as they were being filled, the sample being dried, burned in trial kiln, and ground. From the result of some simple tests of the cement obtained, the sampler was able to judge if either material was in excess, and correct accordingly at the washmill. This method ceased to be of any value with the disuse of backs, as, before the result obtained in the case of any given sample could be known, the slurry sampled would have passed beyond hope

of alteration. In fact, at the present time, when rapid methods of determining carbonate of lime are employed, it is not an easy matter to keep the composition of the slurry flowing from the washmill even fairly constant.

During recent years, not only has greater attention been paid, to the fine grinding of slurry, but means have also been devised for ensuring its more accurate and uniform composition. Generally, the method for effecting this is as follows :—The slurry from the grinding mills is collected in a series of large basins, which are either circular or of oblong form with semi-circular ends, provided with slowly revolving arms for keeping the contents in motion, the oblong form having two sets of arms. When filled, the contents of each basin are tested for carbonate of lime, which, if found correct, are allowed to pass into the collecting tank, from which the kilns are supplied. The
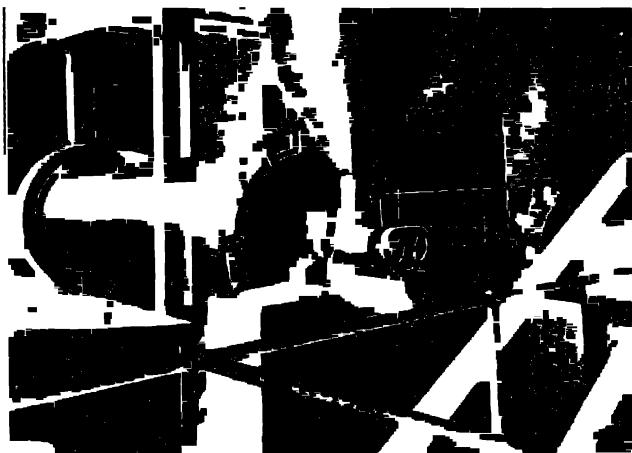


F. L. Smidth & Co.
Fig. 60.—Tube-Mill working in a Slurry Plant.

adjustment to normal composition may sometimes be effected by mixing the contents of one basin with another, wholly or in part. In some cases two basins, usually of smaller size, are provided, one containing slurry much overlimed, the other slurry much overclayed. If the proportions in the large basins are incorrect, the required addition is made from one or other of the smaller ones, and the mixture is again sampled and tested. This operation is repeated if found to be necessary, and the contents of the basins are not finally discharged until they are proved to be of normal composition. The adjustment basin process is due to M. Candlot, who devised it for dealing with the lower chalk and gault clay, both of which are irregular in their content of carbonate of lime. The movement of slurry is usually by pumping, and with suitable pumps delivery may be made at long distances.

Fig. 60 illustrates a tube-mill working in a slurry plant. In modern wet process works the tube-mill has almost invariably displaced the former processes of wet grinding.

**Description of Slurry Plants.**—Methods of preparing slurry have now been generally described, but they admit of many modifications to adapt them to materials differing in character. Two such examples of plants constructed by Messrs. F. L. Smidth & Co. may be described. The first of these is at Klagstrop, a few miles from Malmo, in the South of Sweden. The raw materials are clay and waste soft broken limestone, which thickly overlays valuable beds, now quarried for other purposes. The stuff is fairly pure, but somewhat irregular in composition, it contains hard nodules of carbonate of lime, and much chert and small flint. It is sufficiently soft to admit of washmill treatment, but not so readily as chalk. There are three washmills, one being used exclusively for clay, which is washed separately previous to mixture with the limestone. The other two mills wash the mixture of limestone and clay slurry alternately, one of them being constantly out of use for removal of flints. A large edge-runner mill is placed between them to break down the hard nodules of limestone. It is found that the limestone washed alone does not remain suspended in the water, but that the clay slurry entangles and keeps in suspension particles that would otherwise settle.

Weighed quantities of clay and measured volumes of water are charged into the clay washmill, producing slurry of uniform consistency, which is pumped in measured volume into the combined washmill, the required weight of limestone being added at the same time. The screens are perforated with $\frac{1}{8}$ inch square holes, and the coarse, thick slurry is finished in a tube-mill. From these it flows to three basins provided with rotating arms, in which adjustment is made. Each basin contains sufficient slurry to supply the three rotary kilns for twelve hours. One is always being filled, a second is under test and adjustment, the third is used to supply the kilns. An analysis of cement from this works will be found in the table on p. 87.

The other example is the method in use at the plant of the Austrian Portland Cement Factory at Szczakowa,* in Galicia, for the description of which we are indebted to Mr. W. J. Cooper, who visited it in 1910. The raw materials are very variable, consisting of thin bedded limestone mixed with yellow clay, brown and green mottled plastic clay, and red sandy marl resembling the Devonian marl. Five samples of stone taken at random from two waggons contained respectively 88·06, 95·01, 86·77, 92·70, 96·05 per cent. of carbonate of lime. The stone, all sorts mixed

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* Near Szczakowa three frontiers, those of Germany, Austria, and Russia, met at a point known then as "Three Emperors' Corner." Through taking a wrong train, Mr. Cooper found himself in Russia, and, having no passport for that country, he had some difficulty in getting out of it.

together—some of the beds are only half an inch thick—with its adhering clay is crushed and fed to Kominors by a table feed. The clay and marl are washed together, the water being weighed into the washmill by an automatic weigher, a certain weight of water for each waggon of marl or clay. The thin slurry is lifted by a bucket elevator to another automatic weigher, which empties at frequent intervals, at a rate according to feed of crushed stone for Kominors, into a second elevator; this discharges into the Kominor inlet together with a carefully regulated stream of water. From the Kominors it passes to tube mills through a Trix separator, thence flowing to small mixing tanks like washmills in which harrows move swiftly, keeping the contents in a state of constant agitation. There are two of these tanks, each containing about an hour's grind of slurry. The adjustment is made in these by the addition of clay slurry, the carbonate of lime being previously kept slightly higher than normal to admit of this. There are two Kominors and two tube-mills, which serve to grind, in from twenty to twenty-two hours, sufficient slurry for 190 tons of clinker. This is equal to about 285 tons of raw material, or six and a half to seven tons per set per hour, considered as in the dry condition. The slurry contains 35 per cent. of water, and is very fluid in appearance, thinner than chalk slurry with 40 per cent. From the small washmill mixers it is delivered to large storage tanks with slowly revolving arms for keeping the contents in motion, one for supplying each kiln. From the description of the materials, they would appear to be very unsuitable for producing cement, when compared with those in use in this country, but they do produce a cement of good quality. The following analyses were made of clinker taken at the kilns from the coolers :—

ANALYSES OF SZCZAKOWA CEMENT.

|  | 1. | 2. |
|---|---|---|
| Insoluble residue, . . . . . | ·14 | ·11 |
| Silica, . . . . . . . | 21·54 | 21·25 |
| Alumina, . . . . . . | 7·31 | 7·42 |
| Ferric oxide, . . . . . . | 2·75 | 1·97 |
| Ferrous oxide, . . . . . . | ·56 | ·63 |
| Lime, . . . . . . . | 64·84 | 64·54 |
| Magnesia, . . . . . . | 1·83 | 2·14 |
| Sulphur trioxide, . . . . . | ·28 | ·24 |
| Loss on ignition, . . . . . | ·60 | ·44 |
|  | 99·85 | 98·74 |

At a small plant in England the raw materials are hard crystalline lime-stone and soft alluvial clay, each being of constant composition. The lime-stone is ground dry to a fine powder, and is mixed in the required proportion

with the clay in washmills to produce a thick slurry, which is dried in chambers by the waste gases from the kilns.

**Portland Cement from Marl in America.**—Marl as understood in this country is clay containing a certain amount of carbonate of lime, and sometimes carbonate of magnesia. If the proportion of carbonate of lime is high it is called a chalk marl, if low, a marly clay. The term is very vaguely applied, and is often used to designate substances which contain little or no lime. In the American Portland cement industry it is applied to fresh-water deposits, consisting almost entirely of carbonate of lime, partly of chemical, partly of organic origin, which are found in low-lying lands, marshes, and the beds of wholly or partially dried-up lakes. They consist of deposits from water containing carbonate of lime in solution, and are due to the action of the pond-mussel which abounds in limey water, and which has the power of abstracting lime from it for the formation of the shell. On the death of the animal, the shell sinks to the bottom, forming part of the substance of the marl, the greater number of shells becoming entirely decomposed, the remainder retaining their original form. Deposits of this marl occur in the districts bordering on the Atlantic Seaboard from Virginia to Florida, in Central New York, Michigan, Northern Indiana, Ohio, and in Canada in the districts bordering on Lake Huron, Lake Erie, and Lake Ontario. The deposits vary in depth from a few inches to 30 feet, about 10 feet being considered a fair depth for profitable working. They are sometimes overlaid by peat, or by soil and vegetable growth, beneath them beds of good cement clay frequently occur, particularly in New York and Michigan. The following analyses of some of these marls, all of which are in use for the manufacture of Portland cement, are by Edwin C. Eckel. 1, Rushsylvania, Ohio ; 2, Syracuse, Indiana ; 3, Coldwater, Michigan ; 4, Mosherville, Michigan ; 5, Caledonia, New York ; 6, Warners, New York ; 7, Owen Sound, Ontario ; 8, Marlbank, Ontario :—

|  | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. |
|---|---|---|---|---|---|---|---|---|
| Silica, . . | 1·98 | 1·74 | 1·75 | ·91 | ·40 | ·26 | 1·43 | ·46 |
| Alumina, . . | ·97 | ·90 | 1·57 | ·29 | ·20 | ·10 | ·20 | ·44 |
| Ferric oxide, . | .. | ·28 | .. | .. | ·20 | .. | ·18 | .. |
| Carbonate of lime, | 90·91 | 88·92 | 87·92 | 93·12 | 95·46 | 94·31 | 90·32 | 97·13 |
| Carbonate of magnesia, | 1·25 | 3·65 | ·92 | 2·98 | ·62 | ·37 | 4·36 | ·62 |
| Sulphur trioxide, | ·10 | 1·12 | ·15 | ·31 | 1·70 | .. | .. |  |
| Loss on ignition, | .. | 3·39 | 7·50 | 2·13 | .. | 4·64 | .. |  |
|  | 95·21 | 10·000 | 99·81 | 99·74 | 98·58 | 99·68 | 96·49 | 98·65 |

**Method of Treating Marl.**—The treatment of this material varies considerably and scarcely any two plants adopt exactly the same methods, but, whatever may be the mechanical means employed, great care is invariably taken to ensure the accuracy, fineness, and uniformity of the mixture with clay. The means employed for obtaining the marl are adapted to suit its condition in the bed. In dry situations, mechanical excavators are used both for removing the surface soil or peat, and for extracting the marl, which is deposited in waggons for removal to the works. If the deposit occurs at the bottom of an existing lake, it is obtained by means of dredging, and the loaded barge is then brought as near as possible to the works in order that the contents may be discharged by pumps into the receiving
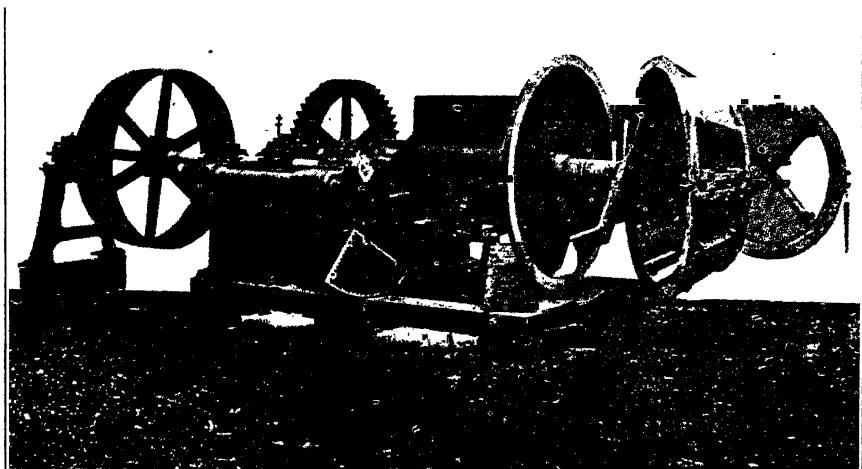


Fig. 61.—Separator for removing Stones and Roots from Marl.

tanks. The same method is employed in swampy ground, in which case a grab-dredger is used. In these circumstances the excavated portion becomes filled with water, and the dredger thus forms its own channel as it moves forward.

When extracted in this way, the marl is frequently too stiff to pump and yet too soft to be readily conveyed in waggons. If waggons are used, the grabs are discharged into them, the roads being laid alongside the channels. It is sometimes possible to arrange that the transport to the works shall be effected by means of conveyor-belts. If pumping is resorted to, the grabs deliver their contents into a pugmill fixed on the barge, and sufficient water is added to produce a thick slurry, which is allowed to collect in the bottom of the barge. This liquid slurry is either pumped through a

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pipe-line, arranged on trestles, passing from the barge to the receiving tank in the works, the pipe-line being continued forward as the excavation proceeds, or a pipe is laid from a fixed point to which the barge is brought, as in the case of dredging from a lake.

On arriving at the works the first operation is to clear the marl from grass, roots, and stones. A machine for effecting this, made by the Bonnot Company, is shown in the illustration, Fig. 61.* It consists of a hopper, which will contain from 1 to 2 cubic yards of marl, placed upon a powerful screw conveyor, which forces the marl through perforated plates, the refuse being discharged from the bottom.

The washmill is little used in America. The mixture of marl and clay is effected by various methods, one being by grinding under heavy edge-runners working in a large pan. This method breaks up the lumps of travertine that are often present in the marls. The final grinding is in tube-mills or by rock emery millstones. The finished slurry is collected in tanks provided with slowly revolving arms to avoid settlement. In some cases the contents are kept in motion by the admission of compressed air, for which purpose a number of small pipes from the main are inserted so as to reach nearly to the bottom of the tanks. The contents are tested, and any required adjustment of proportions is made. The slurry, which often contains as much as 60 per cent. of water, is finally pumped to the tanks that supply the rotary kilns.

* *The Rotary Kiln.* By Lathbury and Spackman. Philadelphia, 1902.

# CHAPTER XII.

## PREPARATION OF THE MIXTURE OF PORTLAND CEMENT RAW MATERIALS BY DRY METHODS.

CONTENTS.—Origin of the Dry Process—Use of Lias Materials and Hard Limestones —Drying the Raw Materials, Rotary Driers—The Tower Drier—Grinding the Raw Materials—Use of Silos—American Practice with Hard Limestones—The Treatment of Soft Materials—Preparation of the Raw Flour for the Kilns—Briquetting.

**Origin of the Dry Process.**—By this method, as mentioned in the previous chapter, the mixture of raw materials is obtained in a fine state of division by dry grinding. It originated in this country, and in quite the early days of the Portland cement industry was employed for dealing with the lime-stones and shales of the lias formation which, from their nature, did not admit of treatment by the wash-mill process then in use for soft materials. In *Die Portland Cement Fabrikation*, by A. Lipowitz, Berlin, 1868,* a dry method is described, and the process is referred to by Dr. Michaelis in *Die Hydraulischen Mörtels*, Leipzig, 1869. It will be remembered from what has been said in the preceding chapter that the hardest materials may, by the use of modern appliances, be treated by the wet process, while it is obvious that generally soft materials may be treated by the dry. Thus, as regards their preparation, any materials suited for the manufacture of Port-land cement may be dealt with by either method, but if the subsequent calcination is to be effected in fixed kilns, the dry process, all things being considered, is the most suitable. This subject will be again referred to when we deal with kilns. The materials generally treated in England by the dry process are those from the lias deposits, although other limestones are to some extent in use. The nature of the lias materials, and the system of manufacture adopted for dealing with them, may be briefly considered before passing on to a general review of the whole subject.

**The Use of Lias Materials.**—The lias formation consists of layers of impure limestone of varying thickness, parted by seams of shale or clay —the total thickness of the latter beds generally considerably exceeds that of the stone. As regards contents of carbonate of lime, the layers of stone vary considerably ; in some cases they approach very closely to that required for a cement mixture. Complete analyses of typical lias limestones have

* English translation by W. F. Reid, in *The Manufacture of Portland Cement*, by Henry Reid. London, 1868.

been given on p. 12, and in the following table are the results of partial analyses of 24 layers or " floors " of stone from a quarry in the Midland counties, the partings consisting of clay. In any one selected lias quarry the percentage composition of the clay in the layers of stone may be taken as being representative of all the others. This is not true of the shales and clays which are very irregular in their composition. Some are high in magnesia, while others often contain sulphur combined with iron as iron pyrites to such an extent as to unfit them for cement making. Analysis No. 1 is that of the top layer of stone.

| No. | Silica. | Oxide of Iron. | Alumina. | Carbonate of Lime. | Carbonate of Magnesia. |
|------|---------|---------------|----------|--------------------|-----------------------|
| 1. | 13·30 | 2·89 | 4·08 | 77·52 | 1·23 |
| 2. | 14·20 | 3·08 | 4·36 | 74·71 | 1·13 |
| 3. | 12·14 | 2·64 | 3·73 | 78·41 | ·98 |
| 4. | 11·63 | 2·53 | 3·57 | 79·45 | 1·24 |
| 5. | 11·04 | 2·40 | 3·40 | 79·92 | 1·46 |
| 6. | 11·17 | 2·43 | 3·43 | 79·39 | 1·40 |
| 7. | 13·11 | 2·85 | 4·13 | 76·29 | 1·36 |
| 8. | 10·13 | 2·20 | 3·11 | 81·69 | 1·40 |
| 9. | 10·15 | 2·27 | 3·12 | 81·05 | 1·54 |
| 10. | 10·78 | 2·34 | 3·31 | 80·49 | 1·24 |
| 11. | 14·06 | 3·05 | 4·32 | 74·81 | 1·25 |
| 12. | 11·03 | 2·40 | 3·41 | 80·22 | ·91 |
| 13. | 10·16 | 2·22 | 3·13 | 81·82 | 1·40 |
| 14. | 12·44 | 2·70 | 3·83 | 77·14 | 1·05 |
| 15. | 11·71 | 2·54 | 3·58 | 78·47 | 2·22 |
| 16. | 13·31 | 2·90 | 4·09 | 76·37 | 1·72 |
| 17. | 12·81 | 2·78 | 3·91 | 75·53 | 2·91 |
| 18. | 11·73 | 2·56 | 3·60 | 78·49 | 1·34 |
| 19. | 9·75 | 2·13 | 3·00 | 80·87 | 2·31 |
| 20. | 10·30 | 2·24 | 3·17 | 80·30 | 1·86 |
| 21. | 10·64 | 2·31 | 3·28 | 78·97 | 2·01 |
| 22. | 10·74 | 2·33 | 3·32 | 79·39 | 2·05 |
| 23. | 10·08 | 2·18 | 3·13 | 81·21 | 1·42 |
| 24. | 15·98 | 3·47 | 5·11 | 70·53 | 1·17 |

With such materials as these, the preparation of a mixture of uniform composition is not a difficult matter. It will be observed that the percentage of carbonate of lime in all of them varies but little from that required for a normal cement mixture, and all that is necessary, therefore, is to grind them together with sufficient clay to bring the percentage of carbonate of lime to about 76 per cent. Owing to the close approximation of these limestones to cement mixtures, and the extremely intimate natural admixture of the carbonate of lime and clay, which is far more perfect than anything which can be produced artificially, cement made from them may safely contain 1 or 2 per cent. more lime than if made from an artificial mixture of carbonate of lime and clay. The preparation of a uniform mixture is not always so easy a matter as in this case. The following table gives the

percentage of carbonate of lime in the successive layers of another quarry, also in the Midland counties. It will be noticed that in this case the proportion of carbonate of lime in the stone is higher than it was in the previous example. The partings between the floors are entirely composed of shale of varying degrees of hardness; those containing the highest percentage of carbonate of lime are invariably the hardest. The line of separation between stone and shale is not, however, very sharply defined. Adhering to the stone, but separating easily from the shale, is a layer of somewhat intermediate material of very irregular composition, from 1 to 2 inches in thickness; this is locally known by the workmen as " scull."

| Floor. | | | | Percentage of $CaCO_3$. | Floor. | | | | Percentage of $CaCO_3$. |
|---|---|---|---|---|---|---|---|---|---|
| No. 1, | . | . | Stone, | 75·20 | No. 5, | . | . | Shale, | 51·71 |
| ,, 2, | . | . | Stone, | 83·12 | ,, 6, | . | . | Stone, | 88·22 |
| ,, 2, | . | . | Shale, | 56·87 | ,, 6, | . | . | Scull, | 68·54 |
| ,, 3, | . | . | Stone, | 85·00 | ,, 6, | . | . | Shale, | 49·02 |
| ,, 3, | . | . | Scull, | 78·39 | ,, 7, | . | . | Stone, | 84·49 |
| ,, 3, | . | . | Shale, | 39·86 | ,, 7, | . | . | Scull, | 69·59 |
| ,, 4, | . | . | Stone, | 86·15 | ,, 7, | . | . | Shale, | 51·34 |
| ,, 4, | . | . | Shale, | 48·59 | ,, 8, | . | . | Stone, | 81·83 |
| ,, 4, | . | . | Shale, | 50·60 | ,, 8, | . | . | Scull, | 77·13 |
| ,, 5, | . | . | Stone, | 88·14 | ,, 8, | . | . | Shale, | 48·42 |
| ,, 5, | . | . | Scull, | 69·65 | ,, 8, | . | . | Shale, | 58·12 |

The system of manufacture generally adopted was briefly as follows :— The layers or floors of stone were stripped off one by one, cleared of adhering shale and clay, and were brought into the works, where they were stored in sheds, each floor separately, this being necessary in consequence of their varying chemical composition. The shale or clay, usually only a small quantity being necessary, was dried on heated floors. The weighed quantities of each material were crushed and ground together to a fine powder, which was pugged with water into a plastic state, and dried on heated floors, or sometimes in chambers heated by the waste gases from the kilns. It was finally broken into rough lumps and burned with coke in intermittent kilns. This was a slovenly and wasteful process, as the dry product, unlike the dry slurry prepared from chalk and clay, which is hard and tenacious, was very friable, disintegrating, and causing much dust and small material in the kilns, which impeded the free passage of the air required for combustion. It gave place to a brick-making process, the stream of material issuing from the pugmill being cut off into bricks which after drying were sufficiently dense to be easily handled and loaded into the kilns. Later, semi-dry pressed bricks came into favour. These were denser, and much more easily dried, while if continuous kilns were employed the bricks could be taken to them direct from the presses without previous drying.

Many of the English works using lias materials now employ rotary kilns, the preparation being in some cases by the dry, in others by the thick slurry

process. With either process, the shale or clay adhering to the limestone is not in itself an objection. By the dry process the material, even if clean limestone, is now usually dried before grinding, and in the case of stone with adhering shale or clay this would at the same time be dried. By the wet process, as will be seen by the description in the previous chapter of the slurry plant at Szczakowa, its treatment would present no difficulty. But, if its presence would result in an overclayed mixture, it would be necessary to add a purer limestone, which might not be convenient, or to remove the shale or clay, and this is sometimes effected by mechanical means. The waggons of stone as quarried are dumped into a long revolving cage of great strength constructed of longitudinal bars arranged with suitable spaces. It is inclined at such an angle from the horizontal as to allow the lumps of stone to travel down it. As they pass down they are cleaned by the action of the lumps falling and rubbing against each other, and against the bars. The refuse falls through the spaces between the bars, the stone is delivered sufficiently clean at the end of the cage. At one plant using the lias beds, which here occur with only thin partings of shale and clay, the whole face of the quarry is blasted down, the debris is lifted by a steam shovel, and discharged into the revolving cage.

**Drying the Raw Materials, Rotary Driers.**—The raw materials must be in a perfectly dry condition before grinding, and if dried in rotary driers must be previously crushed. For hard materials the crushing may be effected by machines of the rotary or gyratory type, or by the reciprocating jaw machine; softer materials, such as chalk, shale, or damp marl or clay, are crushed by toothed or corrugated rolls or by perforated pan edge-runner mills. Soft, wet clay is somewhat difficult to deal with mechanically. Perhaps the best treatment is by rolls set widely apart, in which long project-ing teeth or cutters are inserted at intervals.

With some materials the mixture may be made before drying, but usually they are dried separately, and mixed afterwards. Drying may in some cases be wholly or partially dispensed with. At a plant using lias materials, and producing 600 tons of cement a week, the cleaned stone is stored in sheds and not further dried; the clay is dried in a rotary drier. The mixture of limestone and dry clay is made at the crusher, the grinding is by ball and tube mill. At the Portland Cement Fabrik Rüdersdorf, near Berlin, in 1903, the limestone was conveyed from the quarries to the works by aerial ropeways, stored under sheds and used without further drying, the clay was dried in rotary driers, the grinding being by under-runner millstones. This method served for an output of 2,300 tons of cement a week, but we are not able to say if any change has since been made. The Californian Portland Cement Company for their first plant, built during the closing years of the last century, avoided artificial drying altogether. The materials were calcite and clay. The first-named was on the site of the works, and

was used as quarried, the clay field was about 30 miles distant. The clay was ploughed up in patches during the summer, and, after exposure to the hot, dry atmosphere until dry, was brought to the works by rail, and stored in bins of 5,000 cubic yards capacity. The plant was a comparatively small one for America, it made about 500 barrels of cement per day, and we do not know if the process was entirely satisfactory. A recent plant erected by the same company is equipped with rotary driers for all the materials.

Whether artificially dried or not, the materials should be perfectly dry before grinding, as even a small percentage of moisture considerably reduces the output of the mills. Some materials are very hygroscopic, and it is not only necessary to dry them, but to grind them as soon as dried.
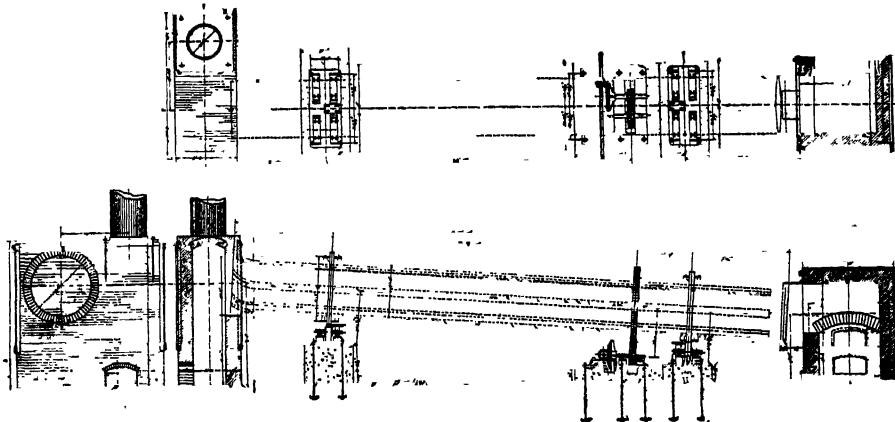


Fig. 62.—Plan and Section of Lathbury & Spackman's Rotary Drier.

The rotary drier in its simplest form is a slightly inclined revolving cylinder from 30 to 40 feet in length, and from 5 to 6 feet in diameter. The products of combustion and the heated air from a furnace constructed at the lower or discharge end pass through the cylinder in direct contact with the material to be dried, which is continuously fed in at the upper end, at which the gases are carried away by a chimney, having previously passed through a chamber in which is deposited the dust from the dry material which they carry with them. Various devices adapted to the material under treatment are employed to bring it into contact with the hot gases during its passage through the cylinder. For drying limestone, steel channels which lift and drop the material from one to the other are found effective. A plan and section of a drier of this type are shown by Fig. 62, and two similar driers in

course of erection by Messrs. Lathbury & Spackman are illustrated in Fig. 63.

In some forms of this apparatus the cylinder is enclosed in brickwork, the hot gases first circulate round it and then pass through the interior



Fig. 63.—Lathbury & Spackman's Driers during Erection.

in the opposite direction to that in which the material is travelling. This form of rotary drier is suitable for materials containing small percentages of water, and it is frequently heated by hot air drawn from the clinker coolers of rotary kilns.

A rotary drier, used to a considerable extent in the cement industry, is that of Ruggles-Coles. It consists of an outer shell of heavy steel plate encircled by two steel tires which rest on bearing wheels; on these the whole construction—which is arranged at a slight inclination.towards the discharge end—revolves. It is driven by a shaft, and a pinion which engages with a geared wheel surrounding the shell. Side rollers are provided to take the end thrust. Within this shell a second one of smaller diameter, also made of heavy steel plate, is securely fixed to it concentrically. The inner shell extends beyond the outer one at its upper end, and passes through a fixed head in which, with, of course, the whole apparatus, it revolves; it is connected with a flue from a furnace. The material to be dried is delivered into the space between the shells at the upper end, and travels to the lower one. The gases from the furnace pass through the inner shell in the same direction,



Fig. 64.—Ruggles-Coles Drier.

and return through the material to be dried, being drawn in by an exhaust fan which discharges into the air and is generally fixed near the furnace. Appliances adapted to the material to be dried lift it as it passes along, and drop it upon the hot outer surface of the inner shell. On reaching the end, the dry material is lifted by scoops and discharged through the centre of the end plate. This drier is illustrated by Fig. 64.

The gases from the furnace enter at a temperature of about 760°. During their passage through the inner shell they part with most of their heat and leave it at about 120°. At this point external air is admitted to reduce their temperature still further, and after passing through the drying material the gases finally leave at about 40°. The following are actual results obtained from this drier :—*

* From a Pamphlet, " Rotary Drying Machines." Electro-Metals, Limited, London.

| Material Treated. | Granulated Slag | Clay. | Cement Rock. | Coal. |
|---|---|---|---|---|
| Calorific value of fuel used, | 14,320 | 12,240 | 14,100 | 13,400 |
| Fuel consumed per hour, lbs., | 502 | 550 | 360 | 308 |
| Amount of moisture in material, | 15·25 % | 23·5 % | 2·3 % | 14·01 % |
| Water evaporated per hour, lbs., | 4,158 | 4,166 | 1,852 | 2,746 |
| Water evaporated per lb. of fuel, lbs., | 8·28 | 7·57 | 5·1 | 9·15 |
| Material dried per hour, lbs., | 23,112 | 14,486 | 78,684 | 18,300 |
| Fuel per ton of dried material, lbs., | 43·5 | 76·0 | 9·2 | 33·7 |
| Heat lost in exhaust air, Heat lost by radiation, | 15·5 % | { 14·8 % { 8·8 % | 8·5 % 5·0 % | } 11·3 % |
| Heat used to evaporate water, | 66·5 % | 69·6 % | 40·9 % | 74·6 % |
| Heat used to raise temperature of material, | 18·0 % | 6·8 % | 45·6 % | 14·1 % |
| Total efficiency, | 84·5 % | 76·4 % | 86·5 % | 88·7 % |

By what is known as the "Aero System," these driers are sometimes heated with powdered coal. The pulveriser, a machine of the disintegrator type, is placed in front of the drier, replacing the furnace. The action of the beaters supplies sufficient air, the volume of which can be regulated, to force the powdered coal into a combustion chamber, where it burns like gas. The use of powdered coal as fuel will be dealt with fully in a later chapter on rotary kilns.

**The Drying Tower.**—In this, the material to be dried is delivered at the top of a tower, and is withdrawn at the bottom, meeting in its passage downwards a current of heated air, which is drawn through it by means of an exhaust fan. Fig. 65 shows a section of one form of tower which was devised by F. L. Smidth. It is constructed of two domes of brickwork, one within the other, enclosed by an outer shell; the material to be dried passes down in the space between the two domes. The outer one is surmounted by a cylinder formed of steel plate which passes through it, within it is another cylinder of smaller diameter, into which the material is charged, and which should always be kept full. The exhaust fan is connected by a trunk with the space between these cylinders. Hot air from a furnace, or other source of heat, is drawn by the action of the exhauster into the inner dome and through a number of ports into the material being dried, while cold air is drawn through the openings from which the dried material is withdrawn. This air cools the dried material, and is, consequently, heated in its upward progress. As both this, and the hot air admitted by the ports, if allowed to pass direct to the exhauster, would find the passages of least resistance,

much of the material would be left undried or be only partially dried. To avoid this, an annular channel formed of steel plate, in such a manner as not to impede the downward course of the material, is arranged against the wall of the outer dome. Into this a portion of the heated air is drawn and is discharged at a higher level. By this means heated air penetrates all parts of the descending material, which is thus uniformly dried. The arrows shown in the section indicate the direction of the air currents.

Fig. 66 is an illustration showing two of the three towers of this type at the Skanska Cement Works, near Malmo, Sweden. They are connected by bridges, over which the material is conveyed in waggons, which are drawn
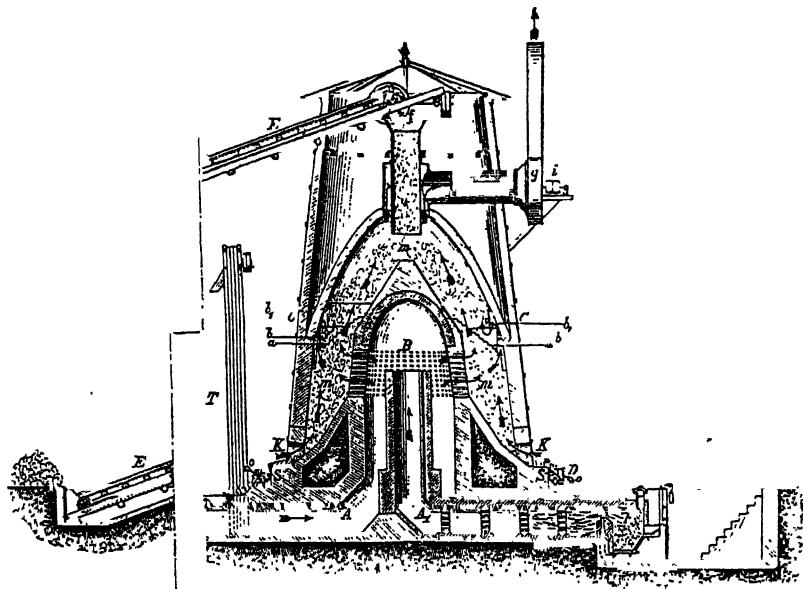


Fig. 65.—Smidth Drying Tower.

up the incline, as shown by the illustration, here reproduced from a photograph, for which we are indebted to Mr. Hallgren, director of the works, who has devised a method of automatically withdrawing the dry material from the towers. Openings, which are regulated by doors sliding in a vertical direction, are arranged round the base, and these discharge the contents upon a slowly revolving flat ring. From this it is swept off into hoppers, which deliver into waggons below, as shown in the left-hand tower of the illustration.

This form of tower is suitable for drying chalk, clay, and chalk marl, and, so long as the hot air can be drawn uniformly through the material

under treatment, it will work efficiently with a moderate proportion of small material, but if the small is in considerable quantity it is best to use the rotary drier. Very wet clay should be stored under cover until it has parted



Fig. 66.—Smidth Drying Towers at the Skanska Cement Works, near Malmo, Sweden.

with some of its water, otherwise it will be liable to consolidate when tipped into the tower and thus obstruct the passage of the heated air.

**Grinding the Dry Material.**—Grinding may be effected by any of the mills described in Chapter IX., all of them are in greater or less use for raw materials. In this country, those most often employed are the tube-mill with either the ball-mill or Kominor for preliminary grinding. In the United States these mills are also in extensive use, in some instances Sturtevant or Kent mills being used as preliminary grinders for the tube-mills. The Griffin and Bradley mills are also much used, while the Fuller mill is meeting with increasing favour, and its use is rapidly extending. As regards fineness of grinding, what has been said in the previous chapter on the fineness of slurry is equally true here, and need not be repeated.

In any system of grinding involving the use of separators, care must be taken to avoid irregularity in the composition of the product. In some of the mills that we have described, the operation of grinding really involves separation, as, for instance, in the Kominor, the Griffin, and Bradley mills, also the Fuller, and the Raymond mill, but they all yield a uniform product from mixtures of material that may differ considerably both in hardness and chemical composition. But in these instances separation takes place within the mill itself, the portion rejected by the screens and in the Raymond mill by the air separator falls back into the grinding chamber as soon as separated ; there is, consequently, no danger of any irregularity in its return. External separation is quite satisfactory, if sufficient care is taken to ensure the immediate return of the portion rejected by the separator to the inlet of the mill, and not to the feed hopper containing a reserve of crushed material. As an instance, we give the following results obtained with the Pfeiffer [*] sieveless ball mill and air separator, the arrangement of which plant is shown by Fig. 39, p. 146. The percentage indicates carbonate of lime.

| Series 1. | Series 2. | Series 3. | Series 4. |
|---|---|---|---|
| 76·75 per cent. | 75·50 per cent. | 76·75 per cent. | 75·25 per cent. |
| 77·00    ,, | 75·25    ,, | 77·50    ,, | 75·25    ,, |
| 76·25    ,, | 76·00    ,, | 78·00    ,, | 74·75    ,, |
| 76·50    ,, | 76·75    ,, | 78·00    ,, | 75·00    ,, |
| 76·75    ,, | 76·75    ,, | 77·50    ,, | 75·50    ,, |
| 76·50    ,, | 76·50    ,, | 77·25    ,, | 76·00    ,, |
| 77·25    ,, | 77·25    ,, | 76·75    ,, | 76·25    ,, |
| 77·50    ,, | 77·50    ,, | 76·50    ,, | 76·50    ,, |
| 78·00    ,, | 77·25    ,, | 76·50    ,, | 76·50    ,, |
| 77·75    ,, | 76·00    ,, | 76·25    ,, | 76·75    ,, |
| 76·50    ,, | 76·50    ,, | 76·75    ,, | 77·25    ,, |
| 76·00    ,, | 76·75    ,, | 76·00    ,, | 77·25    ,, |

Considering the irregular composition of the clay, these results are as

* *Tonindustrie Zeitung,* April 30th, 1910.

uniform as would be obtained by any other system of grinding. The average percentage of carbonate of lime needed is 76·6, and the variation from this amount is not large, as will be seen by an examination of the table. By distributing material, ground as uniformly as this was, layer above layer in silos and withdrawing it by a conveyor at the bottom, the layers would fall together and a product would be obtained varying little, if any, from the normal.

**Silos.**—The construction of silos for containing raw flour must depend entirely on the purpose for which they are required. With raw materials of uniform composition, and in which little variation is likely to occur, they may be used for storing a supply of flour, and, at the same time, serve to equalise any slight irregularities occurring during the operations of crushing and grinding. In this case they are generally of large size, the flour being drawn from them in several places by worms, which all discharge into one mixing conveyor. With irregular materials, it is usual to construct several silos of moderate size, the contents of which may be tested before they are drawn out. By simple arrangements of extracting worms and elevators, these silos may be made to answer all the purposes of the adjustment basins of the wet process. It is thus possible to carry out the mixing most efficiently by continually extracting the flour at the bottom, and elevating, and discharging it again at the top, either while the silo is being filled or afterwards. The contents of one silo, if overlimed, may be mixed with the contents of another that is overclayed, by withdrawing the contents together and discharging them either into a third silo or into the main conveyor. Again, the contents of one silo, if of incorrect proportions, may be drawn out and discharged into another that is being filled from the mills, the material from which is adjusted to correct that from the silo, while, at the same time, the mixture may be perfected by continually withdrawing the contents at the bottom and discharging them at the top during the time that the filling is in progress.

**Automatic Weighing.**—Automatic machines, which we have previously mentioned incidentally, are well known, and are frequently used for weighing the components of cement mixtures. A system of employing them was devised by F. L. Smidth, with the object of enabling an accurate mixture to be made of two materials when the final grinding is by tube-mills. The materials are ground in a dry condition to coarse powders, which are collected in separate bins. Two automatic machines, one for each material, are coupled together in such a manner that the hoppers in which the materials are weighed will only discharge simultaneously, and then only when each of them has received the exact weight of material to which it has been set. The coarse powders are withdrawn from the storage bins by worms, and the machines are under the control of the chemist in charge, who regulates and alone has access to them. A counter attached to each machine shows the

quantity of material that has passed through. The machines discharge into a screw conveyor, which mixes, and at the same time conducts, the coarse powder to the tube-mills, which both grind and effect a very intimate mixture of the ingredients. This system is equally applicable to finely crushed materials for grinding by any other method.

**American Practice with Hard Limestone.**—The manufacture of Portland cement by the dry process from hard materials has attained its greatest development in America; by far the largest quantity of cement made in that country being produced from limestone. The principal seat of the industry is in the Lehigh Valley, Pennsylvania; the limestone which is employed occurs on each side of the Lehigh River, in the neighbourhood of Coplay, and also across the Delaware, near Phillipsburg, New Jersey. This stone forms part of the Silurian formation, and in some cases is a nearly pure carbonate of lime, in others it consists of hydraulic limestone known as " cement rock," containing from about 68 to 72 per cent. of carbonate of lime. This rock is sometimes of uniform composition, but frequently the percentage of carbonate of lime varies in the different beds. A cement mixture is made of the two rocks, and while the method of preparing and grinding differs in details and in the plant employed, the general principle is the same in all the manufactories.

Drying previous to grinding is universal, this being effected in rotary driers after crushing. When each kind of rock is of uniform composition, the quantities are usually weighed at the commencement, previous to crushing. If the composition is irregular, they are roughly crushed, dried, and either very finely crushed or coarsely ground separately, the products being stored in bins for sampling and testing for carbonate of lime. The weighing is effected by automatic machines. The ground material is conveyed from the mills to the hoppers or stock bins supplying the rotary kilns. They are usually constructed to contain sufficient material to supply the kilns for from 24 to 48 hours.

**The Edison Process.**—This is an entire departure from the usual methods. The plant is situated at Stewartsville, near Phillipsburg, New Jersey, and was designed to produce 1,500 tons of cement per day, a commencement being made with half this quantity. The materials are cement rock and nearly pure limestone, and the crushing and grinding are effected entirely by rolls. Each rock is coarsely crushed separately. The first rolls are 5 feet wide and 5 feet in diameter. After passing these, the rock falls successively through three other pairs of rolls, which reduce it to a size of 1½ inches and smaller. The crushed material is carried by conveyor belts to the driers. These are towers heated by coal fires at the bottom, and filled with cast-iron baffle-plates or shelves, down which the material passes. From these towers it is conveyed by belts to storage bins, the cement rock and limestone being still separate. From these bins each material is weighed automatically,

and the mixture is carried by conveyor belts to the fine grinding rolls. The process now becomes a system of grinding and separation. After leaving the rolls, a certain quantity of the material passes in a thin stream in front of the outlet from a blower. Of these there are sixteen, each of which is provided with a box having muslin sides. The fine dust is blown into these boxes, which retain it, the air passing through the muslin. The grit falls upon a belt, and is conveyed back to the rolls for further grinding. The dust, 96 per cent. of which is said to pass a sieve having 40,000 meshes per square inch, is conveyed from the boxes to a floor, on which it falls layer above layer, and is turned over and mixed by a rotating screw. From this floor it is conveyed to the rotary kilns. This process does not seem adapted for giving a product of uniform composition, but it must be remembered that the cement rock, which closely approaches the composition of cement mixture, forms from 80 to 90 per cent. of the whole, and the resulting produce must consequently be more perfectly compounded than if pure limestone constituted the greater part. One of the most disastrous failures we ever knew resulted from the incompetent use of air separators upon a mixture of hard and nearly pure limestone and soft shale.

We have described the Edison plant as it was originally installed, but we have heard recently that separation has been discontinued, the product from the fine rolls being finished in either Fuller or tube-mills.

**The Preparation of the Raw Flour from Limestone and Clay.**—Two methods will be described. Both are in actual use, and may be taken as typical of the best modern practice for dealing with limestone and clay. In the first case, the materials are of regular composition and are fairly pure. The clay is dried in towers; the limestone, which is hard and non-absorbent, is not dried, and both these substances are then crushed together in quantities which are weighed by hand; each mixing, which is turned over with the shovel as fed to the crusher, amounts to about 4 cwts. The grinding is by Griffin mills, and the material passes direct from the crushers to the supply hoppers. These are not large, being only of sufficient capacity to ensure a constant supply to the mills. Any attempt to bulk the crushed material at this stage would result in a product of very irregular composition, as the clay and the fine portion of the stone would have a tendency to separate from, and filter through, the coarse portion, thus giving alternately an over-clayed and an overlimed product. The flour from the mills is collected by screw conveyors, which deliver it into silos.

In the other case, the limestone is of constant composition, while the clay contains a small but varying quantity of carbonate of lime. Each material is dried separately, the stone is roughly crushed and passed automatically from the crushers to rotary driers. It is then ground in ball-mills to a coarse powder, which is elevated and delivered into storage bins. The clay is also dried by rotary driers, crushed between rollers to a coarse powder,

and this is delivered into storage bins, from which samples are withdrawn for testing. From the result of the tests, the proper proportion of clay to limestone is calculated. The coarse powders are withdrawn from the bins by worms, and the required proportions weighed by automatic machines, which discharge into a conveyor that mixes and carries the material to tube-mills ; from these the finished material is conveyed to the bins that supply rotary kilns.

**The Treatment of Soft Materials.**—If the calcination is in rotary, or in chamber kilns, a wet process is usually employed for soft materials, but if burned in continuous shaft kilns they are treated by a dry method. Two works, on the Medway, using chalk and clay, manufacture by the dry process and calcine in shaft kilns. Some of the works in the Cambridge district employ the wet process, using rotary and chamber kilns, others use a dry method and calcine in shaft (Schneider) kilns. The raw materials here are soft chalk marls, which approximate very closely in composition to a cement mixture, and chalk which is used in small quantity to obtain an exact mixture. In America, in the early days of the rotary kiln, it was customary to treat dredged marls by the dry process, a practice abandoned in favour of wet treatment, in consequence of the difficulty and cost of drying the marl. In countries subject to severe winters a wet process must necessarily suspend operations during frost, and, a few years previous to the general employment of the rotary kiln, many plants in Northern Europe, especially those making thin slurry and using backs, changed to the dry process. Some of them have reverted to the wet treatment, preparing thick slurry, and calcining in rotary kilns.

The dry, like the wet, process admits of many modifications in accordance with the nature of the materials, and the ideas or experience of the designer of the plant. We give two instances of the method employed in adjoining manufactories using similar raw materials, which are chalk marls of very irregular composition, the carbonate of lime varying from 65 to 97 per cent. In the first instance, the marls as quarried are weighed in the correct proportions and introduced into an edge-runner mill with a perforated pan. From this mill the mixture passes successively through a rotary drier, rolls to break up any hard nibs, and a tube-mill. This arrangement of pan-mill, drier, rolls and tube-mill, forms one unit of plant. The fine flour from the tube-mills is moistened with a little water in a mixer of the pug-mill type, and is made into semi-dry bricks which are clinkered in Hoffmann kilns.

In the other case, some of the marls are fairly hard, and the system employed is a combination of a wet and a dry process. The hard marls are prepared in the dry way, as described in the previous example, the soft marls are washed to a thin cream-like slurry. Both the dry flour and the slurry are of strictly normal composition. The two materials are mixed in pug-mills to such a consistency as to admit of being made into wire-cut

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bricks, which are dried in tunnels and clinkered in Schneider kilns. It is evident that in preparing the mixture no other care need be taken than to ensure the proper consistency, both materials being normal.

**Preparing the Raw Flour for the Kilns, Brick-making or Briquetting.—** With rotary kilns no further treatment of the raw flour after grinding is necessary. It is conveyed from the mills or silos to the bins or hoppers supplying the kilns. In the state of flour it cannot be dealt with in fixed kilns, and it is usual either to pug and wire-cut, or to compress it into bricks. If limestone forms the whole or a considerable part of the mixture this is not an easy process, as the material does not cohere, and the bricks are soft and friable. With soft and plastic materials, such as chalk, clay, and chalk marls, wire-cut bricks may be made, and are quite satisfactory, and although there are cases in which such bricks are passed directly into shaft kilns without drying, it is usual to dry them, and this is generally done in tunnel driers. These consist of a series of tunnels from 100 to 120 feet in length, through each of which a large volume of air that has been heated by passing through a furnace is drawn by a fan. The bricks, as taken from the machine, are stacked upon waggons, which pass continuously through the tunnels on lines of rails in the opposite direction to the current of heated air. They are thus first exposed to the action of the air leaving the tunnel, which has lost much of its heat, and has become charged with moisture. As the waggons gradually pass onwards they encounter drier and hotter air, until on reaching the farther end the bricks have become perfectly dry and ready for the kiln. The tunnels are kept constantly filled with waggons, each of which remains in the tunnel for 24 hours. One tunnel, 100 feet long with two waggon ways, will dry from 7,000 to 8,000 bricks in 24 hours, the efficiency being stated to be an evaporation of about 13 lbs. of water to the pound of fuel. An early plant of the Coplay Cement Company in Pennsylvania was operated by the dry process with fixed kilns, the raw materials being the hard limestones of the district. The ground material was entirely wanting in plasticity, and a little natural cement was added to give it a slight set. The mixture was pugged and wire-cut into bricks, which were dried in tunnel driers.

With either plastic or non-plastic materials, we prefer to make semi-dry bricks, as they are denser and more easily handled than if made plastic, and they may go direct from the presses to the kilns without drying. It is not clear to whom we are indebted for this process, or where it was first employed. It was very fully dealt with by Henry Reid in his book on Portland cement, published in 1877, in which some types of semi-dry machines were described, but we are not aware if the process was in actual use at that time. We ourselves, after some preliminary experiments with hand-pressing, put it into practice in 1883, on a mixture of lias limestone and shale, not a very favourable material to deal with, as it was wanting in plasticity when

wetted. After many failures, we succeeded in producing bricks that were sufficiently dense to bear handling and stacking, and yet not so much so as to be difficult to burn. If too dense the outside becomes overburned before the centre is fully clinkered, and, in relation to this fact, regard must be paid to both the weight and shape of the bricks. Thin bricks are most suitable, but they may have a fairly large surface area, if about 10 × 5 inches, and from 2¼ to 2½ inches thick they will clinker perfectly throughout. For 3-inch bricks more fuel will be required to clinker their centres properly.
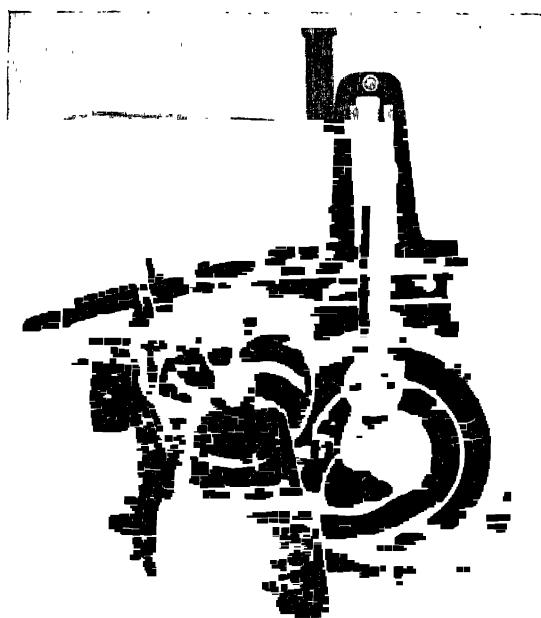


Fig. 67.—Whittaker Semi-dry Briquette Press.

The weight of a brick may be about 8 lbs., for the same dimensions this will vary with the nature of the material and the fineness to which it is ground.

To ensure thorough clinkering, the use of egg-shaped balls, weighing from 5 to 6 lbs. each, has been suggested, and we believe they have in some instances been used. It has been proposed to convey them automatically directly from the presses to the kilns. Obviously such forms cannot conveniently be held in reserve, while bricks may be stacked, and it is advisable to keep a supply of material on the kiln charging-floor to provide for emer-

gencies. A very usual practice, and a good one, is to mix a certain propor-
tion of small fuel, either small anthracite coal or coke breeze, with the raw
flour before pressing. The quantity may be about half of that required
for the calcination of the material.

For briquetting we have used successfully the Whittaker press, which
is employed to a considerable extent in England and abroad for making semi-
dry bricks from shale, and at several English cement works for pressing
raw flour. Fig. 67 illustrates a single mould press which will make 500 bricks
an hour, the brick being delivered lengthways; by a slight alteration it will
make two bricks at one operation, these being delivered endways, the output
then being 1,000 an hour. Abroad, the Dorsten hammer press is generally
used. It is made with either two or four moulds or dies, each brick receiving
three blows from a falling hammer. It is important that the flour should
be uniformly moistened, the quantity of water required varies from 9 to
11 per cent., according to the nature of the material and the fineness to which
it is ground. The mixing may be done continuously by means of an ordinary
paddle blade conveyor.

# CHAPTER XIII.

## FIXED KILNS.

CONTENTS.—The Open Kiln—The Closed or Chamber Kiln—The Johnson—De Michele
—Batchelor and Spackman Chamber Kilns—The Gases evolved from Cement
Kilns—Continuous Shaft Kilns—The Dietzsch—Aalborg—Riisager—Schneider—
Hauenschild—Hotop—Stein—Candlot—Buda-Pest Kiln—The Hoffmann Kiln—
Fuel Consumption and Output of various Kilns.

**The Open Kiln.**—This was the type of kiln originally employed, and its design was evidently based upon that of the lime kiln, but in addition it was surmounted by a tapering chimney or cone to increase the draught. The capacity generally varied from 20 to 30 tons of burned material, the larger size being slightly more economical of fuel. The bottom is provided with a grate of loose bars, upon which alternate layers of coke and dry raw material are laid until the kiln is filled. It is then lighted, allowed to burn off, and when cold the charge is withdrawn. While extravagant as regards the item of fuel consumption, this type of kiln produces clinker of excellent quality. The results of some of our own experiments to determine the exact weight of fuel used per ton of clinker burned in open kilns of 20 tons capacity were as follows :—The material burned was wet process slurry, well dried on flats. It contained 76 per cent. of carbonate of lime, was of uniform composition, and as it left the washmill was of such fineness that all of it passed through a test-sieve having 10,000 meshes to the square inch. It was specially well dried for these trials, and was found on the mean of several determinations to contain only 2 per cent. of water. The coke also was fairly dry. Pieces of moderate size were employed, except in the bottoms, for which larger lumps were picked out. Five brushwood faggots were used in each case to start the fires. In kilns Nos. 3 and 7 all the materials were accurately weighed in and the product was weighed out.

The weight of coke was in No. 3 kiln—

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| In bottom on faggots, | . | . | . | 0 tons | 7 cwts. | 1 qr. | 24 lbs. |
| In layers interstratified, | | . | . | 7 „ | 4 „ | 0 „ | 20 „ |
| On top of kiln, | . | . | . | 0 „ | 7 „ | 0 „ | 0 „ |
| | | | | | | | |
| Total, | . | . | . | 7 tons | 18 cwts. | 2 qrs. | 16 lbs. |

This kiln yielded 19 tons 2 cwts. 2 qrs. of good clinker, and 6 cwts. 3 qrs. of yellow ; and, therefore, to produce 1 ton of clinker, the coke required was 8 cwts. 1 qr. 5 lbs. As the mean of repeated observations, 50 bushels of gas coke fresh from the works weighed 21 cwts., and, therefore, 8 cwts. 1 qr. 5 lbs. are equal approximately to 19¾ bushels. The coke cost 2½d. per bushel, and, therefore, the cost of the coke for burning 1 ton of cement was almost exactly 4s.

In No. 7 kiln, with the same careful observations, 7 tons 17 cwts. 2 qrs. 16 lbs. of coke produced 19 tons 7 cwts. 2 qrs. of clinker, and 2 cwts. 1 qr. 12 lbs. of yellow ; the coke used per ton of clinker was thus 8 cwts. 15 lbs., say, 19·36 bushels, which cost about 4s., as before.

In a third trial, the weights in which were arrived at by an average, each ton of clinker needed 18·66 bushels of coke, or, say, 3s. 11d. per ton, for the fuel for burning.

The mean of these results gives a consumption of 8 cwts. 12¾ lbs. of coke to the ton of cement, or, as it is usually expressed, 40·57 per cent.—that is, to 100 parts of cement 40·57 of coke.

**The Closed or Chamber Kiln.**—Open kilns are now rarely employed. While the shape of the burning portion remains practically unchanged, the open tops are dispensed with, the products of combustion being by various arrangements made to dry sufficient material for the succeeding charge. Kilns of this type were formerly in very general use in this country for dealing with the slurry of the wet process, which was lifted and distributed by pumps upon the floors of the drying chambers, but the adoption of the rotary kiln has made slurry drying obsolete. Some of the closed kilns most generally employed will be briefly described.

**The Johnson Chamber Kiln.**—This kiln was the first to utilise efficiently the waste gases from the open kiln, thereby dispensing with the use of coke ovens and drying flats. Previous attempts by leading the gases along flues that heated floors on which slurry was spread met with little success. The Johnson system consists in the addition to the kiln at its upper level of an arched chamber of the same width as the kiln, and of such a length that the floor area will hold sufficient slurry to serve when dry as a full charge for the kiln. The chimney or dome is dispensed with, and the chamber is of sufficient height for men to work in it conveniently. As will be seen from the illustration, Fig. 68, this chamber is simply a short tunnel interposed between the kiln and a chimney. Each chamber may be from 12 to 14 feet in width and from 80 to 100 feet in length, the dimensions depending upon the capacity of the kiln. The floor is slightly inclined, falling towards the kiln, so that the layer of slurry may be deepest in the vicinity of the kiln, where the greatest heat is found. The products of combustion pass over the upper surface of the slurry, which may vary in depth from 10 to 12 inches close to the kiln to about 3 or 4 inches at the far end of the chamber. The
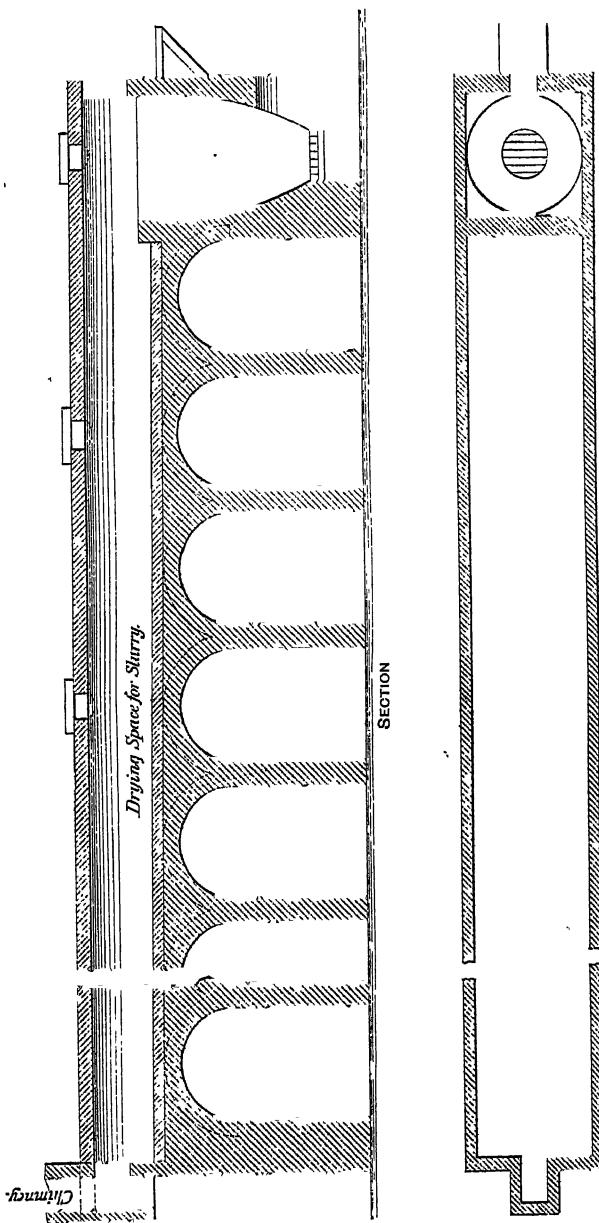
Fig. 68.—Johnson's Drying Chambers.
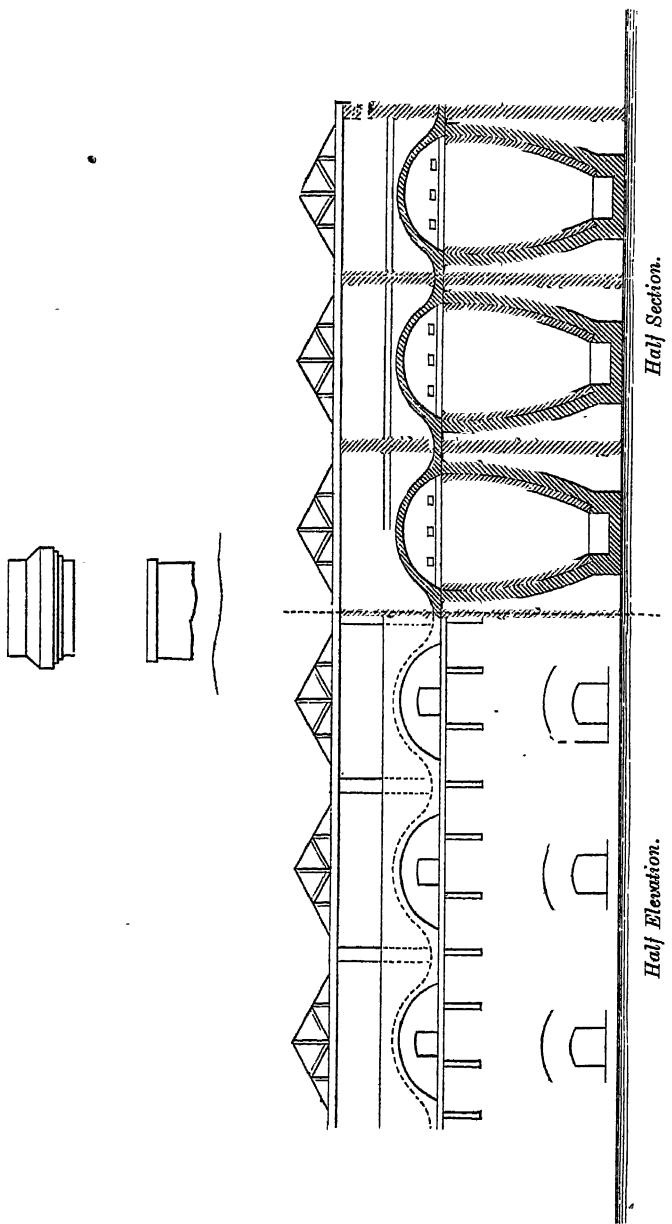
Fig. 69.—Michele's Patent Chambers.

Half Section.

Half Elevation.

use of these chambers involves considerable chimney power, and frequently several kilns are connected with one lofty shaft.

As compared with the open kiln, Mr. Johnson gave us the following results obtained with his chamber kiln :—65 chaldrons of gas coke costing 10s. 6d. per chaldron burned 133 tons of cement in six kilns, equal to about ½ chaldron per ton. In a well-managed works on the open kiln system 20¼ bushels were required for 1 ton of cement. For 133 tons this is equal to 75 chaldrons. The comparative fuel cost works out as follows :—Two-thirds of the coke used in the open kilns being made in coke ovens under the drying flats and costing 16s. 10d. per chaldron.

| | | | |
|---|---|---|---|
| In open kilns, two-thirds of 75 chaldrons of coke from ovens at 16s. 10d. per chaldron, . . . . . | £42 | 1 | 8 |
| In open kilns, one-third of 75 chaldrons of gas coke bought at 10s. 6d. per chaldron, . . . . . | 13 | 2 | 6 |
| The open kiln system of drying and burning costs for fuel, | £55 | 4 | 2 |
| The Johnson kiln system costs for 65 chaldrons of gas coke at 10s. 6d., . . . . . . . . | 34 | 2 | 6 |
| Balance in favour of the Johnson kiln for 133 tons of cement, . . . . . . . . | £21 | 1 | 8 |
| Balance in favour of the Johnson kiln for 1 ton of cement, | 0 | 3 | 2 |

A chaldron of coke = 15 cwts., and contains 36 bushels weighing about 47 lbs. each. On these figures the fuel used in the Johnson kiln = 37·7 per cent., in the open kiln 42·4 per cent.

It should not be assumed that the fuel consumption in the Johnson, or indeed in any form of chamber kiln, is less than in the open one. In the example given the coke may have differed in quality, while the draught in the chamber kilns was probably better. The kilns at Mr. Johnson's works are connected with a chimney 300 feet high, having a diameter of 9 feet at the top.

**Michele's Chambers.**—In these, the chambers are of less height than those in the Johnson system, the exterior surfaces of the arches, as well as the floors of the chambers, are used for drying, and by this means shorter chambers may be used. The arches are of very light construction, and are covered by a roof to protect them from the weather. It is necessary to spread the slurry on these arched surfaces by hand, and this must entail a considerable amount of labour. The illustration, Fig. 69, shows an elevation and section of a series of chambers.

**The Batchelor Kiln.**—This is shown in Fig. 70. At the back of the burning portion two or three arched chambers are arranged, one above the other. The products of combustion pass into and circulate through the chambers, and are finally discharged into a chimney at the rear end of the kiln, one

*Section to show Chambers.*

*Plan.*

*Section.*
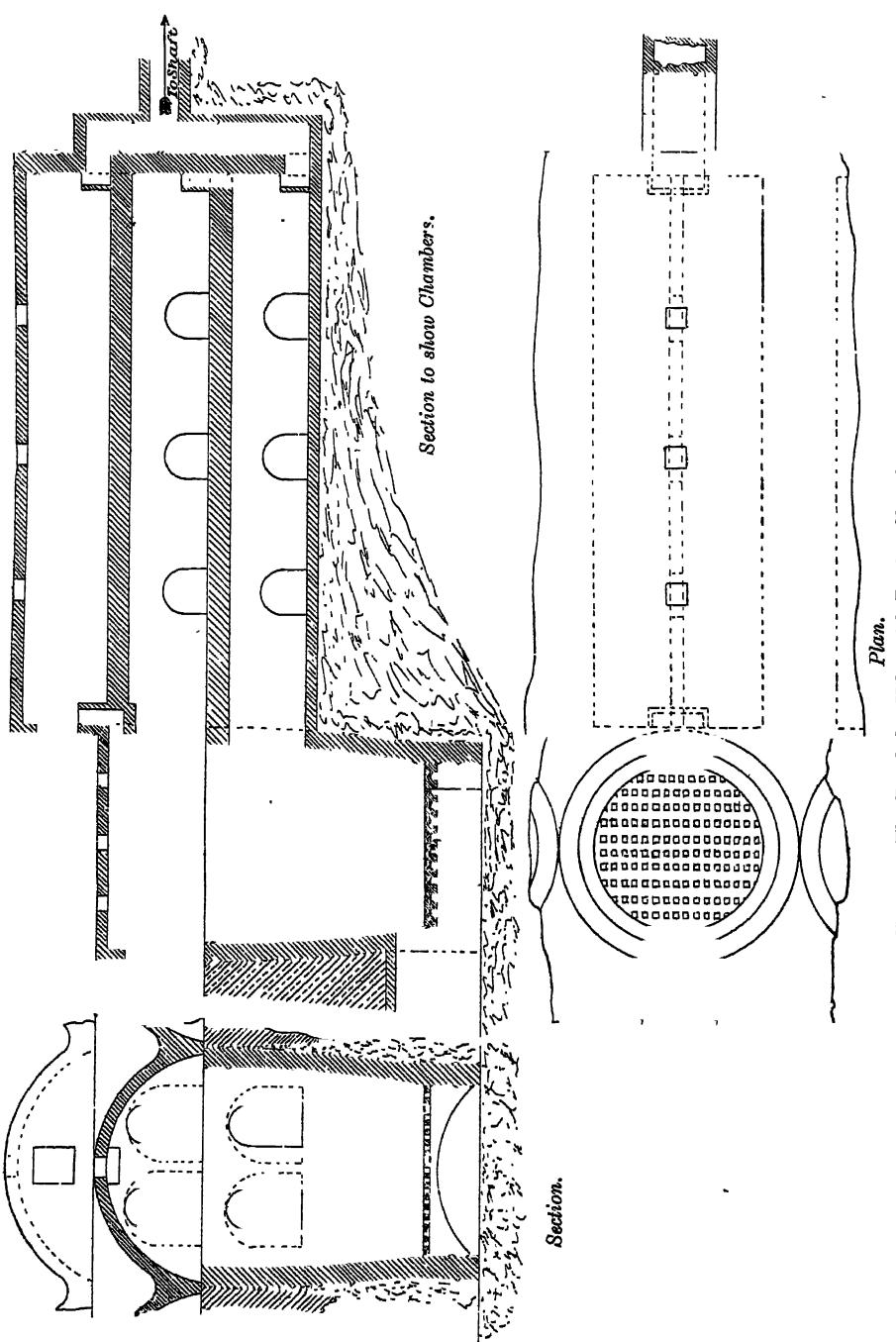
Fig. 70.—The Batchelor Kiln, with Drying Chambers.

powerful chimney frequently serving for a block or group of kilns. The slurry is contained in the spaces between the arches covering the uppermost chamber, from which it is admitted to the floors by passages. This kiln may be lit as soon as it is charged, the covering of the floors going on during the early stage of burning when little heat is passing off.

**Drying Chambers for Raw Material in the Form of Bricks.**—When the cement compound is made into bricks or blocks, the drying chambers attached to the kilns on the plan arranged by ourselves, and shown in the illustration (Fig. 71), may be used with considerable advantage. It will be seen that, in this invention, the chambers are rectangular in form, and are placed alongside the kilns at such a level as to be most convenient for the loading operations. The kilns, which are of the usual type, with a conical chimney, are burnt in the ordinary way with interstratified fuel. The orifice of the dome is provided with a damper, and when the charge is in full fire and the combustion is nearly completed, the upper damper is closed, and the dampers in connection with the underground flues leading to a lofty chimney are raised. By this means the hot gases from the kiln are drawn through the chamber, passing downwards in special flues, constructed in the contents, to orifices in the floors of the drying chamber, which will be seen in the section at A B. The heat of the kiln in cooling is found in practice to be amply sufficient to dry the contents of the chamber, which may conveniently be semi-dry bricks produced by means of any of the machines at present employed for the manufacture of bricks of this kind. The size of the chamber is calculated to furnish a full charge for the kiln, and there are suitable openings both for filling the chamber and for loading the kiln. It will be expedient in arranging for the use of chambers of this kind, which are very economical in working, to place the brick machines at such a level that the bricks, as soon as they are pressed, can be wheeled into the chamber, and stacked in position.

**The Gases evolved from Cement Kilns.**—In certain localities where cement works have been established in the midst of a residential population, and where kilns are used of the types previously described, the fumes evolved during the process of burning the cement, and the smoke from the drying floors and chimneys, have caused more or less nuisance, and have been objected to by the inhabitants. It may, therefore, be as well to consider briefly the grounds for these complaints, and to show how these evils may best be avoided or mitigated. In this enquiry we cannot do better than avail ourselves largely of the able report by Mr. A. Blaikie on "Cement Works in Kent," which will be found in the *Twentieth Annual Report on Alkali, etc., Works for the Year* 1883. The inspector states that "for the purpose of ascertaining the character of the kiln gases emitted, and of tracing any changes that might take place in them from day to day as the kiln burnt out, a number of analyses were made of washings of gases taken

Scale. $\frac{1}{16}$ inch = 1 Foot

SECTION AT A.B.

SECTION AT C.D.　　　SECTION AT E.F.
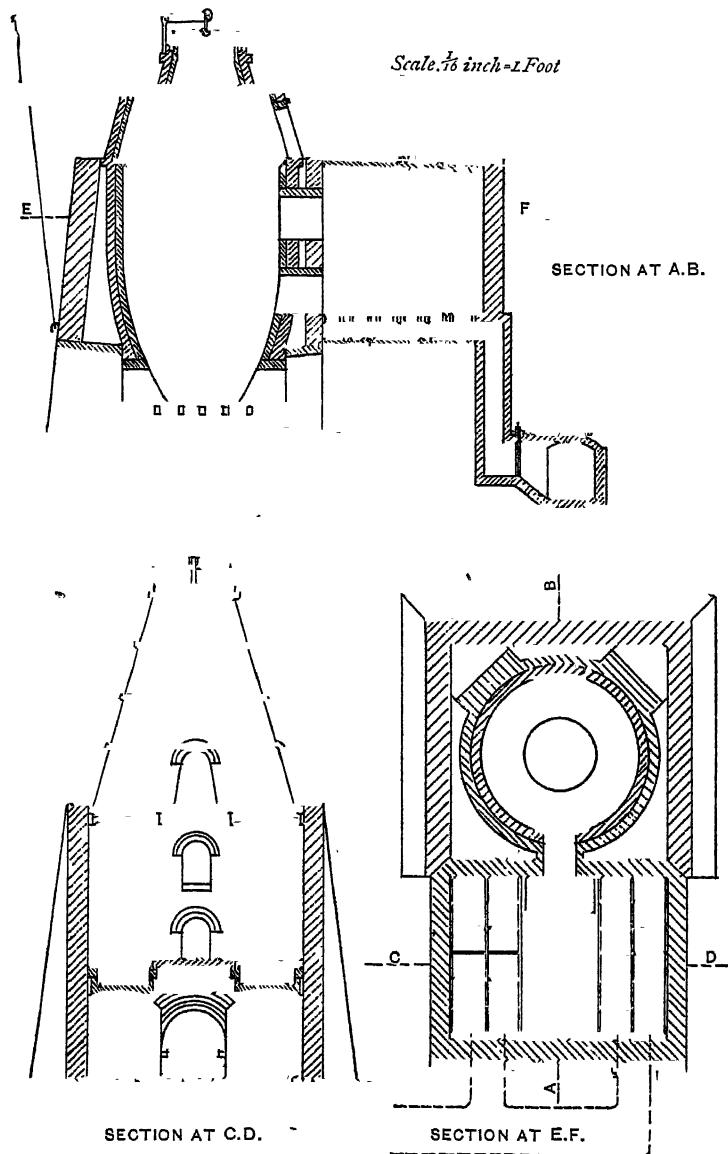
Fig. 71.—Spackman's Drying Chambers.

both from the tops of open kilns and from the flues or chambers of close kilns." He points out that "the usual time required for burning out a large kiln is from three to four days. On the first day a white vapour is given off, which consists practically of nothing but moisture, almost no solid matter or smell being present. It is, however, in some states of the weather, very dense. On the second day, as the heat gets up, the smell is often rank and offensive ; a smell of burning organic matter is given off by the slip, and there is also some smell from the coke. This vapour is white and very heavy; it contains a quantity of solid matter, and is usually slightly alkaline, as the gases from the fire passing through the upper layers of dried slip are neutralised and carry away fine particles of chalk. On the third day, sometimes not till the fourth, the kiln is at its greatest heat and beginning to burn out, the vapour being very much lighter and less dense. It has much less smell than the vapour on the second day, but contains much more volatile matter, chiefly chlorides and sulphates of the alkalies, and it has been found that the quantity of chlorides in the washings always increases with the increase of solid matter. The sodium chloride is derived from the water used in preparing the slip, which, as a rule, is very salt, and the potash is probably liberated from the clay (which contains about 0·6 per cent.) by the action of the chalk. During the later stages the amount of the carbonic oxide is large, and to those close by, and inhaling it, poisonous. The gases are also slightly (in most cases very slightly) acid." Mr. Blaikie shows that the nuisance is generally more acute in the case of common open kilns than in those which are provided with a chamber on the Johnson system, or which discharge their gases into flues for drying the slurry on various principles which he describes—the plans of Messrs. Burge, White & Glover, and Margetts. In all these latter kilns there must of necessity be a lofty chimney, which causes the gases to be diluted and dispersed. He traces no evil effects on vegetation arising from the fumes caused by cement works, but he says :—" Near one works, some years ago, there was a fine group of elm trees, and these have all been killed since the coke ovens were erected." He notices, on the other hand, the beneficial effects of these works in causing the disappearance of ague, though we think it is more than doubtful whether there is any connection between the manufacture of cement and the gradual decrease in the prevalence of this disorder. It is often stated that the vapours and fumes evolved from lime kilns have a good effect upon phthisic and consumptive patients, but we have never seen any statistics which can be quoted in support of either of these allegations.

**Continuous Shaft Kilns.**—The kilns we have previously described have been entirely of the intermittent type, the products of combustion from the open kilns being wasted, those from chamber kilns being employed to dry the slurry for the succeeding charge. The consumption of fuel is usually

about the same in both cases, but it is occasionally higher in closed than in open kilns, this being due to restricted draught. At an early period of the Portland cement industry attempts were made to burn the open kiln con-



END VIEW

SECTION

PLAN
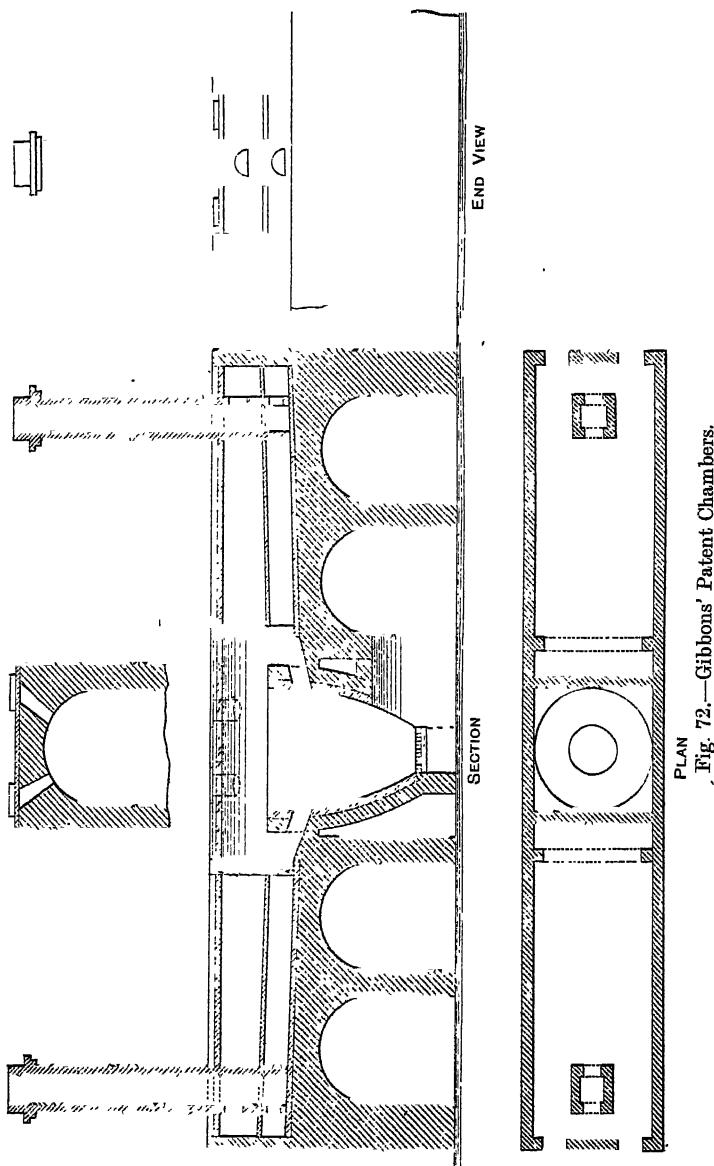
Fig. 72.—Gibbons' Patent Chambers.

tinuously—-clinker being drawn from the bottom at intervals, while, as the charge consequently lowered, dry slurry and coke were added at the top. Thus the waste gases assisted in the calcination of the slurry, which was thrown on as soon as the fire showed signs of coming through the upper-most layers. By burning continuously a considerable saving of fuel may be effected, as in the intermittent kiln much heat is lost in heating the cold walls and, in charging, a greater proportion of fuel is required in the lower layers than above, but the method met with only partial success. The shape of the kiln, broad and low and contracted at its lower portion, was unsuitable. If, as was often the case, the clinker attached itself to the walls of the kiln, and hung up or bridged, it was generally necessary to allow it to cool down, and to empty and restart the kiln.

A continuous kiln to work with drying chambers was designed by R. A. Gibbons, and is illustrated by Fig. 72. The hot gases pass both over and under the slurry in the chambers, which are used alternately, the contents of one being discharged into the kiln while those of the other were drying. It could not have been an economical kiln, as the hot gases, instead of pre-heating the material to be calcined, must have been largely used in the drying chambers. We saw one of these kilns working at Northfleet, and, whatever its advantages or disadvantages may have been, it was producing very fine clinker.

Continuous kilns were long employed at a plant on the Medway for burning a light Portland for plasterers' use, which went principally to the London market. It was not an engineer's cement, and, to produce it, the consumption of fuel was very moderate, the clinker being sintered rather than vitrified. With care in charging there was little danger of bridging or adhesion to the walls. These kilns are still in existence, and are, we believe, working, having been reconstructed in accordance with modern continuous kiln practice.

Attempts at continuous burning having generally proved unsuccessful, a modification known as "topping" was sometimes practised. As soon as the fire had reached, or nearly reached, the top of the charge, successive layers of dry slurry and coke were added, as the fire travelled upwards, until the kiln was full. By this means, a considerable saving of fuel and a larger output was obtained from each kiln, as during calcination the charge of raw material and coke contracts to about half its original bulk, thus allowing room for the extra material, added after the first charging, which itself contracts as the burning progresses.

With the introduction of chamber kilns, either continuous burning or topping, offered at that time little inducement to manufacturers by the wet process. As a set off to the saving of fuel in the kiln the slurry had to be dried independently of it, and, in face of the cost of fuel for this purpose, and for the labour required for handling, it was found less

costly to burn the extra fuel in the kilns and to move the slurry by pumping.

Improved methods of drying, and the increasing cost of fuel, resulted in much attention being given by inventors to the construction of vertical continuous kilns, which, from their small diameter, usually from 7 to 8 feet, combined with their considerable height, which is generally about 40 feet from the floor level to the base of chimney, are frequently called shaft kilns. In these kilns the raw material, usually in some form of briquette, and the fuel are charged in at the top and clinker is withdrawn at the bottom, the operation being a continuous one.

The clinkering zone should be maintained as nearly as possible at a constant level, and as near the working level of the kiln as it can be arranged. Cement material when heated in the kiln to the required temperature, softens, and is liable to weld together and attach itself to the walls. This is especially the case if there is a considerable weight of material above the zone of greatest heat. If adhesion to the walls occurs it is necessary to lower the charge until the adhering masses are entirely exposed, and to break them away from the walls by the use of long bars—a very troublesome operation. When once lumps commence to form they rapidly increase in size by accretion, but a skilful burner can detect them at a very early stage and get them off, and it may be mentioned that the successful working of kilns of this type requires intelligent care and attention on the part of the burners. Before reaching the clinkering zone, the air becomes heated to a high temperature by passing through the cooling clinker, and it is necessary that it should have a uniform and unrestricted passage through the contents of kiln. These kilns are usually arranged in groups or rows enclosed in a building in which floors are placed where required. Some of the most important continuous kilns will now be noticed.

**The Dietzsch Kiln.**—Prominence may be given to this, which was the first successful continuous shaft kiln. It has been, and is still, extensively used, but while very economical as regards fuel consumption, the labour costs are high, and it requires careful and skilful management. It may be described as consisting of four sections :—First, at the base is a cooling chamber for the reception of the clinker after it has been calcined in the firing chamber, which forms the second section of the kiln. Above this chamber is a level hearth constituting the third section, and above this hearth is the preheating chamber, in which the supply of raw material is gradually heated by the waste gases from the firing. This is the fourth section of the kiln. The arrangement will be understood from the diagram (Fig. 73), which illustrates two kilns, built back to back ; one being shown in section, the other in elevation. Here A is the pre-heating chamber, into which the raw cement mixture is charged through the doors situated at E. As all the waste heat of the kiln passes through this chamber to reach the chimney

above it, the material becomes heated to redness before reaching the hearth B. The fuel—small coal of good quality—is introduced through the furnace doors, F, and the material from B is transferred by means of flat shovels
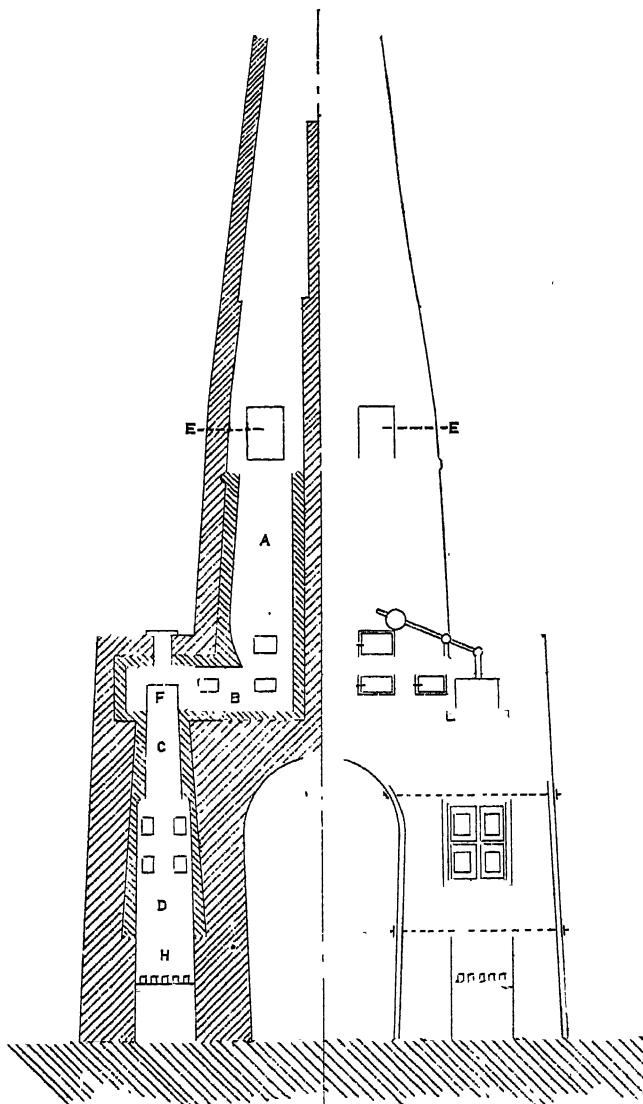


Fig. 73.—The Dietzsch Kiln.

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to the calcining portion C.  The calcined material is drawn out at regular intervals through the bars, H, and the operation of charging is repeated as the contents of C sink.  Openings are provided in D for the purpose of inserting bars to break up any large lumps that may have formed, and, above the firing holes, for breaking away masses of clinker that may attach themselves to the walls of the calcining chamber C. The process of calcining may be observed through the doors at F, and the fuel can be placed where inspection shows it to be required, while cold air entering at the bars is heated by passing through the hot descending clinker, and arrives at the clinkering zone at a high temperature, thus producing intense combustion.  The fuel is consequently utilised to its greatest advantage, as the waste gases give up their available heat to the contents of the pre - heating chamber.  The separation of this section of the kiln from the calcining chamber avoids the danger of compressing the clinker when in the softened condition, by the weight of the material being preheated.  It is claimed that in this kiln 3 cwts. of small bituminous or coking coal will burn 1 ton of cement, and, if well managed, there should be no visible smoke.  According to the size, the output from a double kiln may vary from 20 to 30 tons in 24 hours.  This kiln is adapted for burning lime, for which purpose it has been extensively employed.

The Aalborg Kiln.—This is a shaft kiln, in which the clinkering zone is greatly contracted.  It consists of an upper preheating chamber of the full diameter of the shaft, a central combustion chamber or crucible of reduced diameter, and below this a cooling chamber, which is again widened out
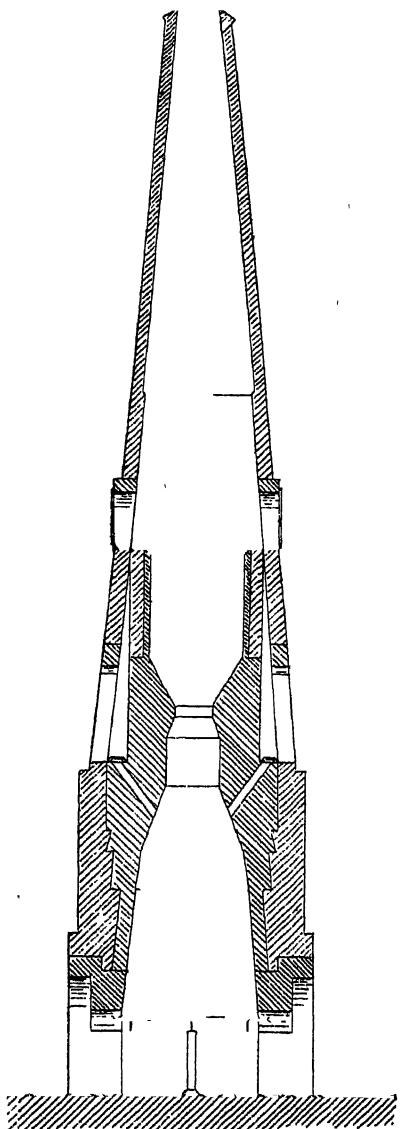


Fig. 74.—The Aalborg Kiln.

to the full diameter of the shaft. This lower chamber is slightly conical in vertical section, with the larger diameter downwards, so as to facilitate the withdrawal of the clinker. The kiln is shown in vertical section by the diagram, Fig. 74. The raw material, in brick form, is charged through the openings at the base of the chimney, and descends to the crucible by gravitation as clinker is drawn out. Openings for the introduction of the fuel are placed at intervals round the kiln, and slant downwards so as to deliver the coal below the clinkering zone. When not in use they are closed with iron covers. In this kiln Portland cement is successfully burned with coal alone, and it is stated that the weight of the coal needed is from 12 to 15 per cent. of the weight of the finished cement, the output being about 14 tons in 24 hours. The labour costs are moderate, and are obviously less than is the case in the Dietzsch kiln, as, after charging, the raw material is not again handled.

**The Rüsager Kiln.**—This is generally called the " R " kiln. In cross-section it is of oblong ellipsoid form, and is shown in vertical section through each diameter by the diagram, Fig. 75. Extending through the kiln is a passage carried on arches, in the floor of which are openings for inserting the fuel and for observing the progress of the burning. The raw material, in moulded form, is charged through the openings at the base of the chimney into the spaces at each side of the passage, in which it is preheated, from whence it descends by gravitation to the clinkering zone, as clinker is drawn out at the bottom. In the calcining section, holes are provided for inserting bars to break up any large lumps that may form. The walls are constructed with a cavity, which communicates with the interior of the kiln, a little distance above the bars, and with a flue encircling it at about the level of the clinkering zone ; this communicates with the external air. By the action of the draught of the kiln, air is drawn into this flue and downwards through the cavity, passing into the kiln in the heated state. By this means the inner wall is kept cool, thus reducing the risk of adhesion of the semi-fused cement material to the lining. The fuel used is small coal.

**The Schneider Kiln.**—This kiln is a plain cylindrical shaft 40 feet high, divided into two sections, the upper one 19 feet high by 7 feet 3 inches in diameter, the lower one of slightly larger diameter and 21 feet high. The upper section, or calcining chamber, is connected with a cavity forming a thin inner shell which is hooped with strong iron belts. It is connected with the lower or cooling chamber by a number of ports, and is closed at the top by brickwork, in which are several openings provided with dampers for regulating the air-current. These openings discharge into a gathering flue which encircles the kiln, from which the heated air passes either into the chimney or into the interior of the kiln at working level. The object of this arrangement is to keep the lining sufficiently cool to prevent adhesion of the calcining material. To guard further against this, a belt of steel plate,

the depth of one charge and about 4 inches less in diameter than the kiln, is suspended by chains, and is lowered before charging. The space between
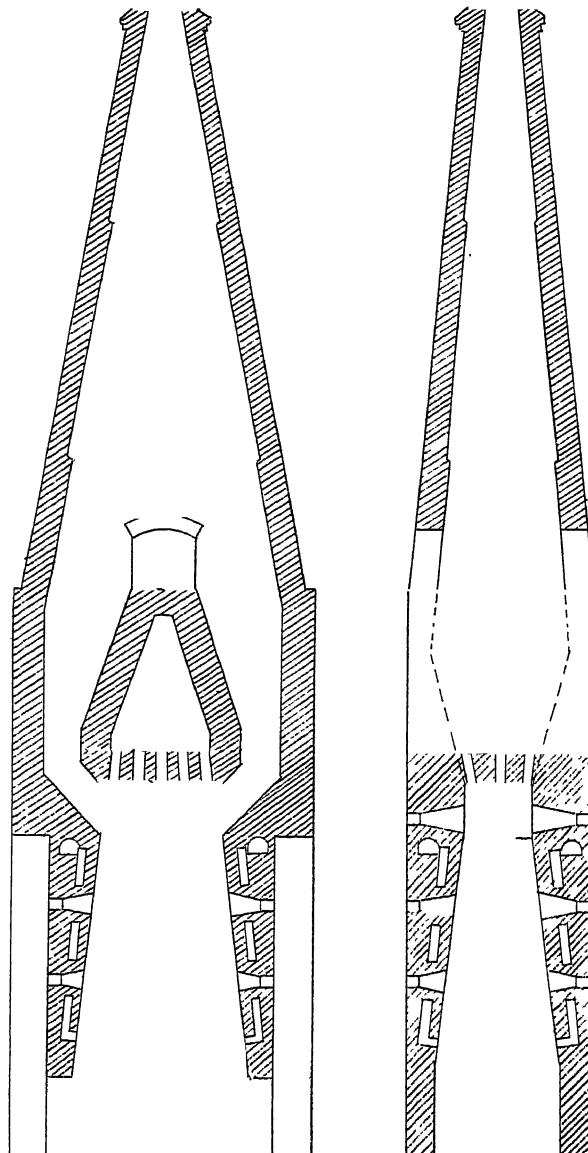


Fig. 75.—Riisager or R. Kiln.

is packed tightly with raw mixture, and the charge is made. The belt is then raised, and the operation of charging repeated. Another method, and one more frequently employed, for keeping the fuel away from the kiln wall, is to place a ring of bricks of raw material edgeways round it, against which the fuel is placed. The fuel used is coke. The kiln is covered by a hood provided with doors through which the raw material and fuel is charged in alternate layers. A chimney, either of brick or of steel plate, may be provided for each kiln, or several may be arranged to discharge into one chimney. The first-named arrangement is the best.

The Schneider kiln has been extensively used in England. It is economical in cost of construction and fuel, and is easy to work. It is especially suitable for dealing with material of a friable nature, direct from the presses without drying, as the method of charging admits of the bricks or lumps being carefully placed, while, except for the gradual lowering of the charge as clinker is drawn out, they are not again disturbed until calcination is complete. The pre-heating is here effected directly above the material undergoing calcination, and care should be taken to keep the clinkering zone fairly high up, and to avoid unduly loading it with raw material— which should be charged in moderate quantities at frequent intervals. The yield of clinker may vary from 10 to 12 tons in 24 hours, and the coke required may vary from 28 to 38 cwts. for this quantity. This kiln, in the original design, was provided with a grate, but it will work quite well with the charge resting on the floor.

**The Hauenschild Kiln,** which has undergone many modifications since its introduction, consists of a cylindrical shaft, constructed of steel plate lined with refractory bricks, and surrounded by a mantle of reinforced concrete at a distance of about 2 feet 6 inches. The air circulating through the space between the mantle and the kiln may, it is stated by the inventor, be supplied under pressure to the kiln. At the base of the shaft is a grate of special construction, which is accessible from all the four quarters of the kiln for the purpose of withdrawing the clinker. In the first design the kiln was provided with a cone or hood, in which were four charging doors for loading purposes, each kiln being provided with its own chimney. In more recent practice, flues from several kilns lead into one chimney. The fuel is coke, and the raw material is pressed into balls of about $3\frac{1}{2}$ lbs. weight, which contain about 6 per cent. of water. The use of powdered lime round the well-cooled wall of the kiln is said to prevent the adhesion of the clinker to the firebrick. It is stated that the fuel required will be from 16·5 to 18 per cent. of the weight of the calcined clinker.

**The Hotop Kiln.**—This kiln is circular in plan, and may be from 40 to 45 feet in height. The top is arched over, but it contains an opening in the centre for the escape of the gases, which pass out thence into the chimney, either built above each kiln, or arranged, as in the case of Hauenschild's

patent, to serve for a group of kilns. At the base of the kiln is a basket-shaped fire-grate, contracted into a central cylindrical ring through which the clinker can be withdrawn. This arrangement prevents the bridging of the clinker, which frequently causes trouble when the draw-holes are situated at the sides, and which sometimes so far prevents the proper descent of the kiln-contents that the kiln has to be cooled down and emptied. It is always found that the centre of the kiln is the hottest part, and this plan of withdrawing the clinker constitutes an important improvement. In all other respects the management and working of the kiln is identical with that of the shaft kilns previously described. The general arrangement will be understood by reference to the diagram (Fig. 76). The dried bricks or slurry, together with the requisite amount of coke, are fed in at the side through openings provided for the purpose, and the burnt clinker is removed through the centre of the fire-grate. The time required for the charge to pass through the kiln is, under ordinary conditions, about thirty-six hours. Six tons of burnt clinker need 1 ton of coke and the yield is from 12 to 14 tons per diem. A special feature of the kiln is the contrivance for preventing the adhesion of the semi-fused clinker to the firebrick lining. Just above the hot zone is a ring of perforated firebricks with small openings through which iron nozzles project into the kiln. These nozzles are supplied with water, under pressure, from a pipe, which surrounds the kiln, and by this means a stream of cold water can be turned on at any time and can be used to cool down the lining. Another advantage of this arrangement is that the steam, which is thus produced, renders the outer part of the clinker adjoining the wall of the kiln more friable and porous, and thus facilitates the emptying process.

**The Stein Ribbed Kiln.**—This kiln differs from the other shaft kilns which we have previously described, in that it consists entirely of iron, built up in a series of rings. The cast-iron blocks which compose the rings are provided with ribs or webs on the exterior, and these are used with a threefold object—first, in order to strengthen the shaft; second, to prevent the distortion likely to arise in the hot zone, owing to the great heat; and third, to avoid the clinging of the kiln contents to the lining, in consequence of the partial fusion of the clinker. The shaft, or kiln proper, rests on four piers of masonry which are united in pairs by means of cross walls to half their height. These piers are further stiffened and tied together by joists, angle irons, and cross ties. Above them is the iron bed-plate which serves as the foundation of the shaft, and on this is erected the superstructure consisting of cast-iron curved rings, which are each kept in place by a small projecting fillet on the inner edge, and these segments key one into the other. They are maintained in position also by their own weight, which is very considerable, and the joints are rendered tight by a coating of slurry. The rings are each 1 foot 8 inches in height, and the diameter of the kiln is made
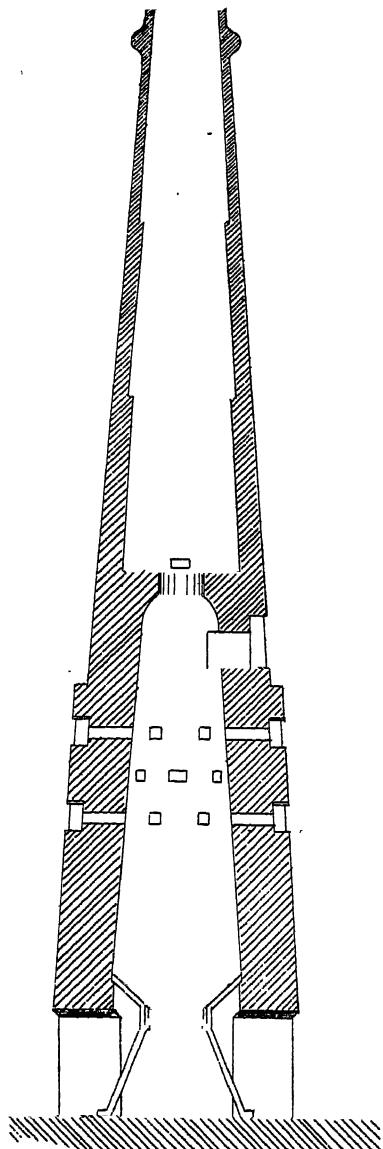
Fig. 76.—The Hotop Kiln—Sectional View.  Fig. 77.—Perpignani-Candlot Kiln.
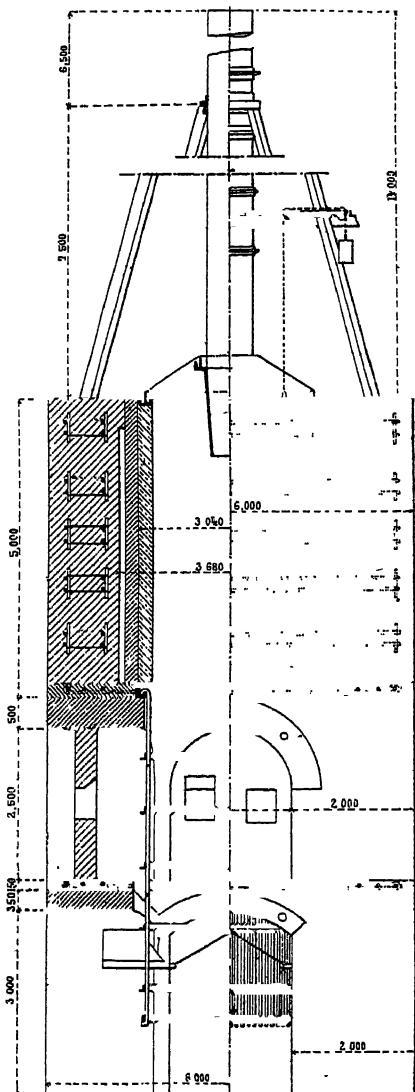
either 6 feet 7 inches or 8 feet 2 inches. The height of the former kiln being 23 feet and of the latter 29 feet 6 inches. Above the uppermost ring is a conical hood formed of stout sheet iron, and this is provided with three or four feeding holes, fitted with doors or shutters. Above the hood is the chimney, which is likewise formed of sheet iron, and which must equal in height the body of the kiln. The chimney should have a diameter varying from 2 feet 3 inches to 3 feet 3 inches, in accordance with the size of the kiln. The top of the chimney is fitted with a damper in order to regulate the draught. In its action this kiln is, of course, continuous, and it is claimed for it that it entirely prevents all tendency in the clinker to adhere to the sides or walls, and that it can be worked with extraordinary regularity. It has been stated that a kiln of this kind has been run for nine months continuously without interruption of any kind.

The yield of a kiln, 8 feet 2 inches in diameter, fed with half-bricks which burn more readily than whole ones, is stated to be 16 tons per diem.

A special form of basket-grate has been designed, also, for this kiln which renders the operation of drawing extremely simple. Though the iron kilns are said to have given such excellent results abroad, some kilns on this principle, which have come under the authors' observation, have not proved altogether successful, and it is evident that great care and skill are needed to burn them with satisfactory results.

**The Perpignani-Candlot Kiln.**—This is illustrated by the diagram, Fig. 77, in half-section, half-elevation, and may be described as a shaft kiln operated by natural induced draught. Externally it is of square form and constructed of masonry or brickwork; the actual kiln being circular in cross-section. The enclosing walls are tied together with iron rods inserted in their thickness. The upper or calcining portion is 21 feet in depth from the charging floor, and 8 feet 6 inches in diameter, and is lined with firebrick. Below this is a circular iron grille, formed of 2-inch square wrought-iron bars with 2½-inch distance pieces. The bars reach to within 2 feet from the floor; they are hooked at the top and hung on an angle iron ring secured to the brickwork. The grille is encircled at intervals with 4-inch angle iron rings, also secured to the brickwork. There is no horizontal grate, the charge resting on the floor, from which it is removed through four openings, one in each wall. Above the drawing-openings are four arched recesses, in each of which are two openings for inspection and for inserting bars to break up any large lumps of clinker that may have formed. These openings are closed by iron doors. The total height from ground level to charging floor is 36 feet. The chimney is of steel plate from 35 to 40 feet high and of 3 feet diameter; it is provided with a butterfly damper, and carries at its lower end a cast-iron mouth of slightly conical form, which reaches to a depth of 3 feet below the level at which the charge is maintained. The open part of the kiln around the mouth is entirely closed by a conical iron cover, through

which the chimney passes. It is flanged on its lower edge, fitting into a channel iron ring which surrounds the kiln, thus providing for a sand lute when required for damping down. The cover may be raised or lowered by pullies and chains, and is balanced by counterweights.

The kiln is set to work in the manner usually employed for any type of continuous shaft kiln. It is filled to within an easy working distance of the charging floor with brick ends or pieces of stone of moderate size. Upon this the fire is started with wood and coke, on which alternate layers of raw material and coke are laid in the usual manner, avoiding placing any near the chimney. The material in the centre is burned by the hot gases which are drawn by the chimney from the sides to the centre. Small fuel—anthracite or coke breeze—may be used, and M. Candlot prefers it. About three-fourths of the quantity required is mixed with the raw flour, the remaining fourth he places round the circumference of the kiln. Instead of bricks he uses flat circular lumps 5½ inches in diameter by 3⅓ inches thick, with a 1½-inch hole through the centre, for facilitating the clinkering of the lump. The mixture is pressed semi-dry with about 8 per cent. of water, the forms passing direct from the presses to the kilns. The amount of fuel required depends as usual upon its quality. It may be from 15 to 20 per cent.

The following test of a Candlot kiln burning artificial Portland cement was made by the Société des Chaux et Ciments de Rivet-Alger, in March, 1906 :—

|  |  |  |  |  |  | Good Clinker. | Underburned. |
|---|---|---|---|---|---|---|---|
| March | 4th, | . | . | . | . | 28,350 kilos. | 450 |
| ,, | 5th, | . | . | . | . | 27,075 ,, | 225 |
| ,, | 6th, | . | . | . | . | 28,070 ,, | 1,215 |
| ,, | 7th, | . | . | . | . | 27,545 ,, | 675 |
| ,, | 8th, | . | . | . | . | 29,480 ,, | 225 |
| ,, | 9th, | . | . | . | . | 28,140 ,, | Nil |
| ,, | 10th, | . | . | . | . | 32,000 ,, | ,, |
| ,, | 11th, | . | . | . | . | Kiln damped down. | .. |
| ,, | 12th, | . | . | . | . | 27,770 kilos. | 135 |
| ,, | 13th, | . | . | . | . | 29,580 ,, | 395 |
| ,, | 14th, | . | . | . | . | 27,710 ,, | 225 |
| ,, | 15th, | . | . | . | . | 28,500 ,, | 360 |
| ,, | 16th, | . | . | . | . | 29,190 ,, | 345 |

Average, 28,625 kilos. of clinker, about 28½ tons daily, underburned 345 kilos., about 6¾ cwts. daily, equal to about 1·3 per cent. of whole. The fuel was small anthracite containing 25 per cent. of ash, the consumption being 16 per cent., or 358½ lbs. per ton. The regularity of the daily output is noticeable, except on the day previous to damping down, on which it is probable that the kiln was drawn down unusually low. On the day following

it was again normal. Adhesion of the semi-fused clinker to the walls is of very unusual occurrence in this kiln, as the central draught tends to prevent overheating. To damp down, the butterfly damper in chimney is closed and the cover is lowered and luted with dust, when it is said the fire can be kept in for eight days without injury.

The Candlot kiln is successfully used for burning lime, especially in France. At the Micheville Steel Works, near Verdun, there were six of these kilns arranged in a row on the side of a hill, the quarry being on a level with the top of the kilns. The stone is a soft cream-coloured oolite of somewhat irregular composition, the carbonate of lime varying from 92 to 97 per cent. The kilns are carried on a raised platform, below which run tram tracks, the lime is raked out from the drawing openings over inclined gratings to separate the small, the lime then falls into trucks.

The result of a test from four kilns extending over nine days in 1909 gave a yield of 31 tons per kiln per day, with a fuel consumption of 4 tons 1¼ cwts. This is equal to 293 lbs. per ton, or 13·1 per cent. The fuel was a mixture of small anthracite and coke breeze. Other results of fuel consumption are given as follows :—

At Champagnole 134 lbs. per ton, equal to 6 per cent., the stone containing 80 to 82 per cent. of carbonate of lime.

At Nice, 224 lbs. per ton, equal to 10 per cent.

At Guerigny, 179 lbs. per ton, equal to 8 per cent., the stone containing from 70 to 78 per cent. of carbonate of lime.

At Bouvesse, 336 lbs. per ton, equal to 15 per cent., the coal containing 35 per cent. of ash. With coke, the consumption was 269 lbs. per ton, equal to 12 per cent. The stone contained 93 per cent. of carbonate of lime.

**Automatic Shaft Kiln.**—In spite of the great development of the rotary kiln, which will be considered in the succeeding chapter, much attention has recently been paid to the improvement of the continuous shaft kiln. Its fuel consumption has always been less than that of the rotary kiln, and it has been further reduced by the use of either forced or induced draught, with a resulting increased output. Other improvements have been in the direction of automatic working, both in withdrawing the clinker and in charging. Automatic methods of charging are simple enough, but for removing the clinker and at the same time breaking it up many devices have been patented. These take the form of rollers, revolving bars, or boring heads. The use of an appliance of this kind enables the clinkering zone to be maintained in one place, while the constant and regular movement of the charge avoids, to a considerable extent, the adhesion of the semi-fused clinker to the walls. Three kilns of this type were working at Buda-Pest early in 1914, and were stated to yield a daily output of 150 tons of cement. The kiln itself is an ordinary cylindrical shaft 8 feet 6 inches in diameter. The fuel is mixed with the raw material, the mixture being

pressed into semi-dry bricks, or other forms, which are automatically distributed over the area of the kilns. The presses, one for each kiln, are placed on the charging floor, which is level with the top of the kilns. The clinker is withdrawn by a revolving grate fitted with a boring head, which is provided with teeth for breaking up the clinker. Compressed air is supplied beneath the grate, which cools the descending clinker and reaches the clinkering zone in a highly heated state. The crushed clinker falls into a funnel-shaped receiver, from which it is removed by a discharging device provided with a valve, so that the exit of the clinker can be effected without loss of air pressure. Motion is imparted to the revolving grate by worm gearing. The speed is usually about one revolution in the hour, but means are provided for varying this. It is stated that 12 H.P. is required for each kiln, which includes that for briquetting the raw material.

Most types of existing shaft kilns can be adapted for automatic working, and on the Continent many have been so adapted. Dr. Muller (Rüdersdorf), as the result of an enquiry, stated in 1919 * that there were in German cement works 240 rotary kilns, 88 ring kilns, 243 Dietzsch kilns, and 384 Schneider and other shaft kilns, 48 of the last-named working automatically.

The Hoffmann or Ring Kiln, which was originally introduced for the burning of bricks, has been employed, chiefly on the Continent, with complete success, for the production of Portland cement clinker. In this country, although it has, as already stated, been from time to time used by Portland cement manufacturers, and has been subjected to lengthy trial, it has, so far as we know, never achieved satisfactory results. It consists of an arched tunnel-shaped firing chamber, which may be circular or oval on plan, or may consist of two parallel tunnels joined by means of semi-circular ends, so as to produce an endless kiln, capable of being subdivided into a series of compartments of nearly equal size by means of cross partitions of a temporary character, which may consist of removable iron screens. From each of these divisions or cells, flues are formed to a central smoke chamber surrounding the lofty chimney. These flues are all of them furnished with dampers, which can be closed, wholly or partly, in order to regulate the draught. The cells have each an external opening in the outer wall of the kiln for loading and unloading, and for the introduction of the above metal screens or partitions. In lieu of wrought iron, it has been for some time past customary to form these screens of paper, as they are fixed in the cool part of the kiln, and serve their purpose for turning the draught until the heat reaches them. Each cell of the kiln is the space enclosed between two such temporary partitions, and the complete kiln may thus consist of from 12 to 20 chambers. When a chamber has been filled with the damp pressed bricks or blocks of slurry, the doorway in the outer wall is carefully built

* *Protokoll der Verhandlungen des Vereins Deutscher Portland Cement-Fabrikanten,* 1919, p. 136.

up and plastered over with loam or slurry to render it air-tight. In kilns of this description, employed for burning cement, each of the chambers is bounded by an arched division, the crown of which is considerably below the top of the arch of the kiln. This mode of construction is essential because of the great amount of contraction which takes place in the cement bricks during the progress of firing. These arches tend, therefore, to drive the flames downwards and direct them towards the centre of the tunnel, in lieu of passing along above the contents of the kiln, in the vacant space just below the crown of the tunnel caused by the sinkage in the clinker.

As an additional safeguard, it is found advisable in Portland cement kilns to contrive openings in the crown of the tunnel, adjacent to each of these dividing arches, so that an additional charge of bricks or blocks, mingled with fuel, can be thrown in during the progress of the firing, in order to compensate for this sinking, and to bring the kiln charge right up to the top of the tunnel. In a well-managed kiln it becomes possible by this means to increase the output some 15 per cent. at the cost of a comparatively small increased quantity of fuel. This kiln is illustrated in Fig. 78. Some manufacturers use two cross-arches in each chamber. In burning Portland, it is necessary to employ a very powerful draught, and experience has shown that two exits to the chimney should be provided, both on the inner and outer side of the chambers, as will be seen in the section at X X.

The bricks are so placed in the chambers as to form continuous flues for the passage of the fire through the mass, and numerous openings in the crown of the kiln seen at Y Y serve for the introduction of the fuel, which is small coal or breeze mixed with coal. The fire passes round and round the kiln in the direction of the draught, and great care and attention must be paid to the feeding of fuel and the management of the dampers, by means of which the draught is regulated. Some manufacturers have been successful in using the Hoffmann kiln with coal alone; indeed it is stated that a kiln at Marseilles is fired with brown coal. Under each of the openings in the vault of the tunnel, it is needful that vertical shafts should lead down to the channels left in the bricks for the passage of the products of combustion, and, as the contents of the kiln shrink together in the progress of the firing, there is a great risk of the collapse of these shafts, or else of the horizontal flues beneath. It is as well to make use of fairly dry bricks or blocks in loading these kilns, and therefore it is usual to subject these bricks to a preliminary drying process; but it is quite possible, with care, to wheel the bricks from the semi-dry presses at once to the chambers, in which state they contain as much as 10 per cent. of water. The heat given out by the clinker in cooling is used to dry and warm up the green bricks, and owing to the very complete utilisation of the
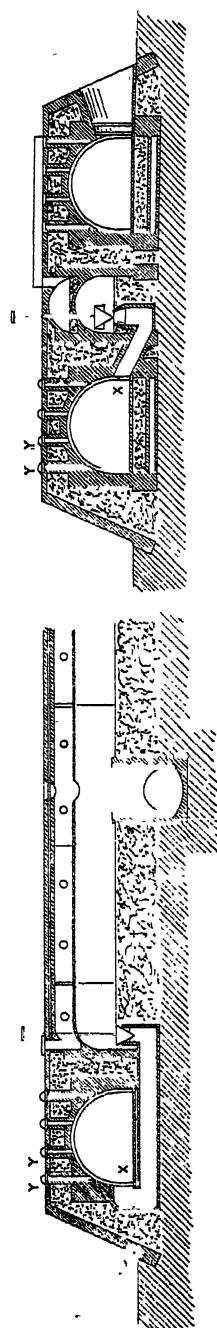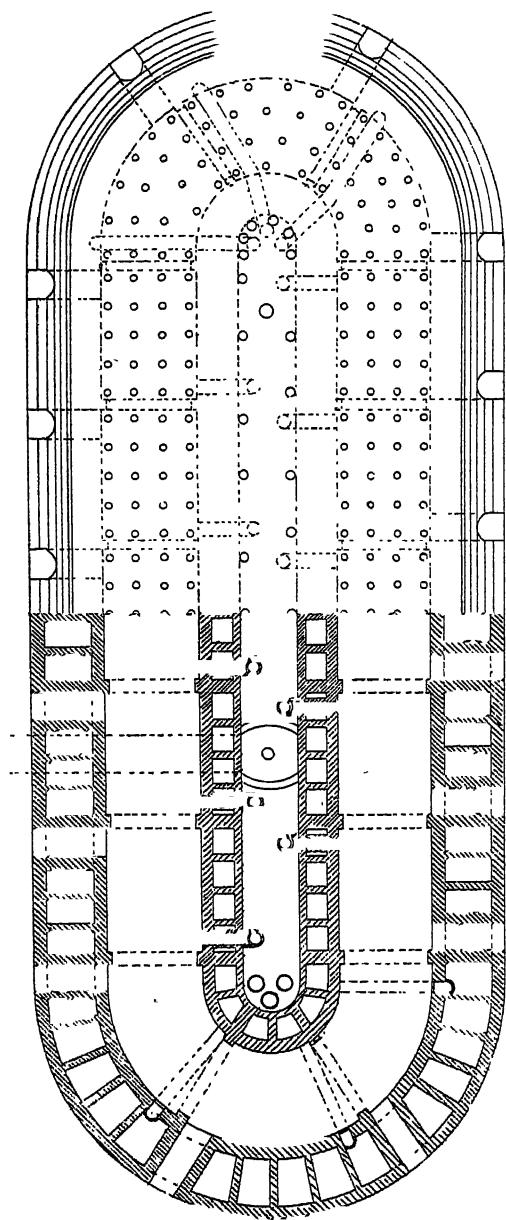
Fig. 78.—The Hoffmann Kiln—Plan and Sections.

| Type of Kiln. | Number of Kilns. | Raw Material. | | Fuel. | | | Output in 24 hours per Kiln. | | | | Underburned. Per Cent. | Cost of Repairs. | | Number of Workmen per Kiln in 24 hours. | Wages, Cost, including Loading and Drawing. Wages per ton. Pence. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | How Prepared. | Water per cent. as put into Kilns. | Description. | Consumption per Ton. | | | | | | | Per Kiln Yearly. Pounds. | Per Ton of Cement. Pence. | | |
| | | | | | Lbs. | P. Cent. | Tons. | Cwts. | Qrs. | Lbs. | | | | | |
| Ring, | 1 | Semi-dry, pressed, | 14 | 60 % coal, 40 % coke, | 470 | 21 | 50 | 3 | 3 | 10 | 10 | 514 | 7·04 | 32 | 24·90 |
| Dietzsch, | 4 | Semi-wet, pressed. | 1·5 | Coal. | 427 | 10 | 8 | 0 | 2 | 13 | 2·5 | .. | 6·34 | 5 | 24·67 |
| Dietzsch, | 2 | ,, | 4·5 | ,, | 460 | 20·1 | 6 | 3 | 3 | 7 | 2 | .. | .. | 4 | 28·19 |
| Aalborg, | 10 | ,, | 3·5 | ,, | 302 | 13·6 | 15 | 18 | 0 | 0 | 2·5 | 54 | 2·81 | 7 | 21·14 |
| Aalborg, | 6 | ,, | 1·5 | ,, | 342 | 15·3 | 10 | 6 | 2 | 20 | 5 | 108 | 7·54 | 6 | 25·02 |
| Schneider, | 6 | ,, | 3 | Coke, | 362 | 16·2 | 15 | 1 | 0 | 18 | 3 | 40 | 1·97 | 7 | 19·03 |
| Schneider, | 6 | ,, | 15·5 | ,, | 447 | 20 | 10 | 17 | 2 | 0 | 1 | .. | .. | 4 | 19·03 |
| Schneider, | 5 | Semi-dry, pressed. | 11 | ,, | 408 | 18 | 9 | 14 | 0 | 9 | 12·5 | .. | .. | 5 | 25·37 |
| Emele, | 1 | ,, | 1·5 | ,, | 380 | 17 | 15 | 1 | 0 | 21 | 1·25 | .. | 4·22 | .. | .. |
| Rüsager, | 6 | ,, | 1·5 | Coal. | 362 | 16·5 | 19 | 4 | 3 | 16 | 1 | 103 | 4·83 | 7 | 19·03 |
| Rüsager, | 7 | ,, | 2·5 | ,, | 355 | 15·9 | 19 | 8 | 0 | 0 | 1·25 | .. | .. | 6 | .. |
| Rüsager, | 7 | , | 6·5 | ,, | 428 | 19·1 | 15 | 18 | 0 | 0 | 1·25 | .. | .. | 6 | .. |
| Schneider, | 6 | ,, | 12 | Coke. | 447 | 20 | 20 | 1 | 2 | 13 | .. | .. | .. | .. | .. |
| Schneider, | 1 | ,, | 12 | ,, | .. | 14·19 | 11 | 14 | 2 | 0 | .. | .. | .. | .. | .. |

products of combustion, it will readily be understood that this system of burning is a very economical one.

The average yield per kiln amounts to about 16,000 tons per annum, but the output depends very largely upon the skill of the burner, and the speed which the fire is driven round. It is usual to work at the rate of filling one chamber every day, which implies, of course, the emptying of a second chamber daily.

**Output, Fuel Consumption, Repairs, and Wages Costs of Continuous Kilns.**—In the table on p. 222 the results, Nos. 1 to 10, are taken from a communication by A. Foss, of Copenhagen, to the Association of German Portland Cement Manufacturers in 1902. Referring to the Aalborg kiln, he gives an example of the improvement in output, and the reduced fuel consumption obtained by careful preparation of the raw materials, and by intelligent handling of the kiln. At a Danish works that commenced to use these kilns in 1890, an output of about 8 tons per kiln in 24 hours, with a fuel consumption of 17 per cent. was considered satisfactory, repairs to kilns being necessary at intervals of three or four months. At the time of his communication the output had reached 18½ tons per kiln, the fuel consumption being 12½ per cent.; repairs were required at intervals of from eighteen months to two years. The remainder of the table is by A. Wirck, and is taken from the *Journal of the St. Petersburg Polytechnic Society* for 1902.

# CHAPTER XIV.

## THE ROTARY KILN.

CONTENTS.—The Rotary System of Crampton—Ransome's Rotary Kiln—Stokes' Rotary Kiln—The Rotary Kiln in America—Ransome's American Patent—The Hurry and Seaman Rotary Kiln—Newberry's Use of Rotary Kiln for Wet Process—The Modern Rotary Kiln—The Lining of Rotary Kilns—Clinker Coolers—The Fuel for Rotary Kilns—The Operation of Burning—Heat Losses, Regeneration of Heat—Comparative Merits of the Dry and the Slurry Process—Separation and Recovery of Dust from the Kiln Gases—Fused Portland Cement.

**The Rotary System of Crampton.**—The proposal to employ a revolving furnace for the calcination of Portland cement originated in this country with Mr. T. R. Crampton, who obtained a patent for his process in 1877. The furnace was fired by powdered fuel injected by compressed air, but it does not seem to have been commercially employed, although at this time revolving furnaces were in use in the alkali manufacture, and had been patented by Siemens in 1869.

**Ransome's Rotary Kiln.**—In May, 1885, Mr. Frederick Ransome patented a rotary kiln for burning cement, which achieved some measure of success, and which was undoubtedly the forerunner of the modern improved system of burning in revolving kilns. The Ransome kiln consisted of an inclined cylindrical furnace, about 25 feet in length, which was carried on roller bearings, and was caused to rotate by means of worm-gearing. The fire-brick lining had a series of projecting courses, so arranged as to form longitudinal ridges. The powdered raw material was fed in by means of a hopper at the upper end, and travelled slowly down the furnace, being turned over and over by the constant revolutions of the kiln, moreover it was caught up and made to fall across the cylinder by the presence of these internal projections. The firing was effected by means of producer gas, which entered the kiln at the opposite end, and yielded large volumes of flame. The cement materials, as they passed forward, were gradually heated to the clinkering stage, and ultimately fell into a pit situated beneath the lowest part of the cylinder. The inventor proposed to burn the cement in the form of a fine powder, and by this means to dispense with the subsequent grinding. His aim was not alone to secure economy in the use of fuel, but he also hoped·by preliminary grinding and sifting of the powdered slurry to turn out a finished Portland cement. He entirely failed to grasp the fact that,

in order to produce a suitable clinker, it was necessary to reach the stage of incipient fusion, and, in its passage through the kiln, the finely-ground cement materials caked together and adhered in a sticky mass to the linings. This caking of the clinker proved the ruin of the process, though Mr. Ransome had other difficulties to contend with. It was found, also, that the finely-divided cement material was carried by the draught right out of the kiln, and had to be intercepted at the exit-end and returned to the feeding hopper. The use of producer-gas, without a regenerator, failed to yield the requisite steady temperature for the calcination process, and when a regenerator was added, it speedily became clogged with the cement powder, carried away into it by the draught. The cement mixture had to be highly limed, and this resulted in a very quick-setting cement, and, owing to the shortness of the tube, it was impossible to utilise the full heating value of the fuel. The working of the kiln was, moreover, constantly interrupted by the balling of the clinker, which collected into lumps and cakes, and stuck, as we have seen, to the linings of the hot zone of the cylinder. After prolonged trials and many costly failures, the Ransome rotary kilns were abandoned as impracticable by English cement manufacturers.

**Stokes' Rotary Kiln.**—A greater measure of success was obtained by the invention of Mr. Wilfred Stokes, who profited by certain of the mistakes of the Ransome kiln, and utilised the heat in a more advantageous way. In the Stokes process, a burning cylinder 5 feet in diameter and 35 feet in length was employed; this was formed of steel plates, resting on two sets of friction rollers, fixed in a cast-iron cradle. This cylinder, which was lined with firebrick, was driven by means of spur gearing, about one revolution per minute, and the waste gas, escaping from the burning cylinder, passed through a second cylinder, 40 feet in length by 12 feet in diameter, set horizontally, and caused to rotate slowly on friction wheels, being driven by worm gearing. The outside of this drum was coated with wet slurry by a dipping arrangement, and the slurry was slowly dried by the hot walls of the drum, to which it adhered. By the time the drum had nearly completed one revolution, the already dried material was scraped off in flakes by a series of chain scrapers, and delivered into the feed-shoot of the burning cylinder. A third cylinder was placed at the lower end of the burning cylinder, and received the red-hot clinker as it issued from the kiln. This cylinder, which was of the same size as the burning cylinder, was provided internally with gills to assist in cooling the clinker as it passed through it, and the current of air driven through the cylinder was used to mix with the producer-gas employed in the burning cylinder.

Although Mr. Stokes encountered many difficulties in working out his invention, most of which he was successful in overcoming, he, too, found the attack of the fused clinker upon the kiln-linings a constant drawback to the satisfactory working of the process; and in spite of the introduction

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of magnesia bricks and bricks made of bauxite, which last proved to be too soft and friable to stand the wear of the kiln, the mechanical defects proved to be insuperable, and the continued use of this form of kiln was rendered impossible.

**The Rotary Kiln in America.**—The Portland cement industry was established by Mr. D. O. Saylor, at Coplay, in Pennsylvania, about 1876, and during the next few years several other plants of small capacity were erected in various parts of the United States. In all of them European methods of manufacture were followed, but although the product was good, it could not compete, as regards cost, with imported cement. These methods involved a considerable amount of labour, and the high cost of this labour as compared with the wages paid in England, and to a still greater extent with those current in Germany, these being the principal exporting countries, rendered the industry unprofitable. The rotary kiln presented a possible solution of this difficulty, and in the hands of M. Pierre Giron, who was the superintendent of the Atlas Cement Works in Pennsylvania, it proved, after many failures and experiments, a success. About 1893 Mr. S. B. Newberry employed rotary kilns 80 feet in length for burning wet slurry; the fuel employed in both these cases was petroleum oil. In 1895 Messrs. Lathbury and Spackman conducted a series of trials, extending over four months, at the works of the Alpha Company, in the use of pulverised coal, as a substitute for crude oil, which previously had been exclusively employed as fuel in all the rotary kilns in America. About the same time the Atlas Cement Company perfected arrangements for the use of coal dust, and now the employment of this material has almost entirely supplanted the oil fuel at first used. It seems impossible to decide to whom belongs the real merit of the present system of using powdered coal, and the patent was refused in the United States Courts to both the rival applicants.

**Ransome's American Patent.**—Ransome's American patent dates from 1886, and it was first used in the United States at a cement works on the Hudson River, near Rondout, by the Atlas Portland Cement Company, and later, with more favourable raw material, at Coplay, in the Lehigh Valley of Pennsylvania. The hard dry materials found at Coplay were in every way adapted for use in rotary kilns, and in course of time, and after great outlay upon experiments, the process, as modified by Mr. T. F. Navarro, proved entirely satisfactory.

**The Hurry and Seaman Rotary Kiln.**—Further improvements in the rotary kiln process were introduced later by Messrs. Hurry and Seaman, who patented their invention in 1895. The chief advantage derived under their patent was economy in the use of fuel, by utilising the heat from the clinker in two auxiliary cylinders. In the first of these cylinders the clinker was received as it fell from the kiln, and a stream of air passing over it became heated and served to ignite the coal dust in the burning cylinder. In a

lower cylinder the clinker, which had been crushed and sprinkled with water, was exposed to a further current of air in order to complete the cooling and drying.

**Newberry : Use of Rotary Kilns for Wet Process.**—While these inventions were being perfected for the dry materials, Mr. Spencer B. Newberry, as we have seen, was carrying on successful experiments at Warners, New York, in the use of rotary kilns for the wet process. He employed a double set of kilns, one being used for drying the wet slurry and the other for the final calcination of the dried material. He afterwards erected a small works at Bay Bridge, near Sandusky, Ohio, and here he again introduced the double system with 40-feet cylinders. He subsequently riveted the two sections into a single cylinder, 80 feet in length, into which the wet slurry was at once introduced, so as to complete the drying and firing in a single operation ; but, after many trials, he concluded that kilns of this great length were not so well adapted for the purpose as shorter ones.

**The Modern Rotary Kiln.**—The Ransome rotary kiln was, as we have seen, 25 feet in length, and the difficulty with its use, both in this country and in America, was that it failed to calcine the raw material before it was discharged from the cylinder ; this kiln was undoubtedly too short. The general principle of the modern kiln is similar to that employed by Ransome. An inclined revolving cylinder constructed of steel plate and lined with refractory material, but without the projecting courses, is carried on roller bearings. The fuel and air supply are admitted at the lower end, the raw material at the upper one. In its passage downwards it is gradually heated, loses its carbon dioxide, and is finally delivered at a white heat at the end of the cylinder as small balls of clinker, varying in size from a pea to a walnut.

In some of the early experiments in America, with powdered coal as fuel, 30-feet cylinders were used, but the flame traversed their whole length, and much of the heat was consequently lost. The length was increased to 50, and then to 60 feet ; this for a time continued to be the standard length, generally with a diameter of 6 feet throughout. In some instances the first 30 feet from the front was of the full diameter, the remainder tapering to 1 foot less at the entrance to chimney, with the object of forcing the heat to the front of the kiln. While this plan reduced the fuel consumption to a small extent, it also reduced the output.

The pioneer of kilns of a greater length than 60 feet was T. A. Edison, who, at his plant at Stewartsville, New Jersey, constructed one 150 feet long with a uniform diameter of 9 feet. It was built up of fifteen cast-iron flanged sections bolted together, and was carried and rotated on fifteen sets of rollers. Although the method of construction with cast iron is not good, and, we believe, has not been repeated elsewhere, the results both as regards fuel economy and output were such a marked improvement on

those obtained from kilns 60 feet long that a gradual increase in the length became general. Lengthening the kiln effects economy of fuel, and at the same time lowers the temperature of the chimney gases, which, however, must be sufficiently hot to ensure adequate draught. The relation between the diameter and the length varies considerably in practice, even in kilns of equal length. Increasing the diameter results in a larger output, but a short kiln of large diameter is extravagant in fuel consumption. The kilns generally in use at the present time are from 125 to 150 feet long, with diameters of from 8 to 9 feet, the output being from 90 to 140 tons in 24 hours. The tendency of recent practice is in favour of longer kilns, and they have been made up to 240 feet long. The lower portion or clinkering zone is sometimes made of greater diameter than the upper part, the result being an increased output with a reduced fuel consumption, as compared with a kiln of similar length of uniform diameter throughout. The following table gives the dimensions of some kilns in actual use :—

| Of Uniform Diameter. | | With Enlarged Clinkering Zone. | |
| Length. | Diameter. | Length. | Diameter. |
| --- | --- | --- | --- |
| 72' 0" | 6' 0" | 108' 3" | 7' 0" to 8' 0" |
| 98' 5" | 6' 7" | 114' 10" | 6' 10" „ 7' 10" |
| 98' 5" | 6' 11" | 142' 8" | 6' 11" „ 7' 9" |
| 108' 3" | 7' 0" | 164' 0" | 8' 0" „ 9' 0" |
| 110' 0" | 7' 0" | *170' 0" | 9' 0" „ 10' 0" |
| 120' 0" | 7' 0" | 200' 0" | 8' 0" „ 9' 0" |
| 120' 0" | 9' 0" | 200' 0" | 9' 0" „ 10' 0" |
| 125' 0" | 7' 6" | 210' 0" | 9' 0" „ 10' 0" |
| 125' 0" | 8' 0" | 230' 0" | 10' 0" „ 11' 4" |
| 125' 0" | 9' 0" | .. | .. |
| 140' 0" | 9' 6" | .. | .. |
| 150' 0" | 10' 0" | .. | .. |
| 164' 0" | 10' 0" | .. | .. |
| 200' 0" | 8' 0" | .. | .. |
| 240' 0" | 10' 0" | .. | .. |
| 240' 0" | 12' 0" | .. | .. |

* Enlarged Portion 40 ft. long.  Oil Fuel.

The shell is constructed of steel plates, which for a kiln 200 to 240 feet long would be ¾ inch thick, and is riveted together with butt straps. It is encircled at intervals by riding rings or tires running on rollers carried by bed plates which rest on massive piers. The tires are not attached directly to the shell, but are recessed into brackets which are bolted to it, on which they are an easy fit to allow for expansion. Their number depends upon the length of the kiln. For one of from 200 to 240 feet, five are sufficient, one near each end, one at the centre near the driving gear, and one between

the driving gear and each end. The early 60-feet kilns were usually supported on two tires. The shell is strengthened by an additional belt of plate at the places where the tires and driving gear are situated. It is set at an incline of about 1 in 25, and is provided with thrust rollers to prevent movement in the direction of its length. It is rotated by an encircling geared ring of somewhat larger diameter than the shell, to which it is attached by plates placed tangentially which act as springs and provide for expansion. The ring is driven by a pinion through a train of gearing, either by a belt from a shaft or preferably by a motor. The speed of rotation will vary according to working conditions; it is usually about one revolution in 65 seconds for a kiln 9 feet in diameter, but provision is made by variable speed gear for slightly increasing or reducing this speed.

The lower end is closed by a hood constructed of steel plate, in which the kiln revolves. It is lined with refractory bricks. The white hot clinker falls into the cooler below. The feed pipe for fuel and air, which are delivered by the action of a blower, should be so designed as to effect their perfect mixture. This enters through the front of the hood, which is also provided with two holes for inspection, and two of larger size for the purpose of admitting bars for removing rings of melted clinker which sometimes form and adhere to the lining of the kiln. It is mounted on wheels, to enable it to be moved back to get at the interior of the kiln. The upper end enters a dust chamber through which the gases pass before gaining the chimney. In this chamber means are provided for arresting the dust carried forward by the gases, an operation that will be described further on in this chapter.

Each kiln is provided with its own chimney, the capacity of which will depend on the dimensions and output of the kiln. It should be capable of maintaining an indraught through the kiln, with provision for its regulation, without raising the exit gases to an unnecessarily high temperature with consequent waste of fuel. As an example, the following observations made in 1910 at the Denmark Cement Fabrik may be cited. The kiln was 158 feet long by 8 feet diameter, enlarged at the clinkering zone to 9 feet, and had a twin coal feed, with the object of obtaining a better flame distribution. It worked with a decided indraught. The chimney was 36 feet high to the point of intake, and 147 feet above, with a uniform diameter of 6 feet. The temperature of the gases as they left the kiln could not be obtained, but the shell was only comfortably warm to the hand at the chimney end, which is unusual, as at this place it is generally too hot to touch. The raw materials were chalk and clay prepared as thick slurry ; the regular output was 140 tons in 24 hours, with a fuel consumption of 27 per cent. of coal as received (and before drying) ; a very good result.

Fig. 79 illustrates a kiln at Felsagolla, near Budapest, by Messrs. F. L. Smidth & Co. It is 230 feet long by 10 feet in diameter, the clinkering zone being enlarged to 11 feet 4 inches.

The fuel for this kiln was brown coal of the following composition per cent. :—

| | | |
|---|---|---|
| Water, | . . . . . . . . | 3·8 |
| Volatile matter, | . . . . . . | 45·9 |
| Fixed carbon, | . . . . . . | 40·5 |
| Ash, | . . . . . . . | 9·8 |
| Calorific value, | . . . . 5,838 calories, about 10,520 B.T.U. |
| „ | when quite dry, . 6,093 „ „ 10,980 B.T.U. |

The output was 190 tons per 24 hours, with a fuel consumption of about 32 per cent.; the slurry contained about 36 per cent. of water. On the addition of a second kiln the total output reached 440 tons per 24 hours, with an increased fuel consumption of from 2 to 4 per cent.
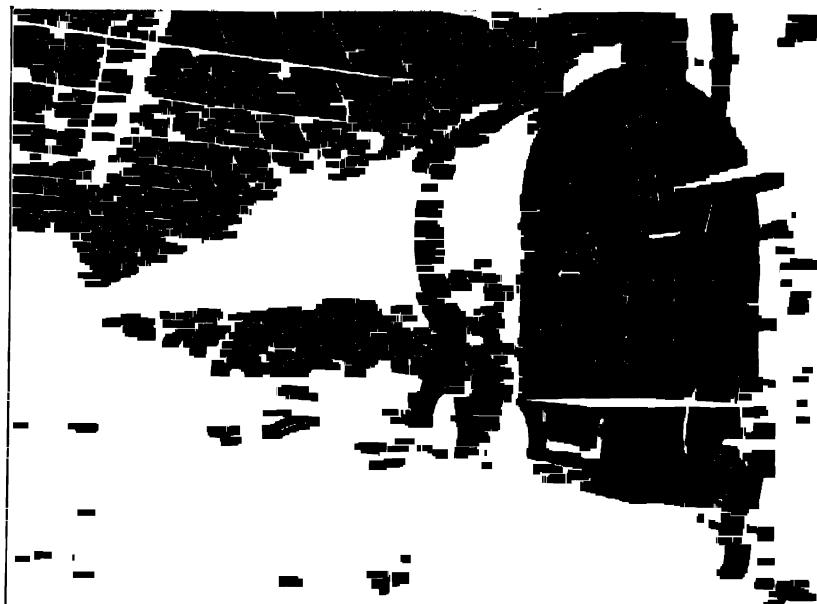


Fig. 79.—Rotary Kiln by Messrs. F. L. Smidth & Co. at Felsagolla.

**The Lining of Rotary Kilns.**—Perhaps no single detail in the use of rotary kilns has been of greater importance than the question of the kiln lining. It was here, as we have seen, that the earlier inventors in all cases failed, and the ultimate success of this system of calcining became assured when this difficulty had been effectually overcome. The firebrick usually employed for refractory purposes contains a high percentage of silica, and behaves as an acid substance in the presence of the Portland cement clinker which is a basic material. At a clinkering temperature these substances react,

and the linings are rapidly attacked and destroyed. The most satisfactory results have been obtained from a highly aluminous brick, containing about 49 per cent. of alumina and 41 per cent. of silica. Attempts have been made to use magnesia bricks, on the assumption that, being themselves basic, there would be no action or adhesion between them and the basic cement clinker. While this is true, they were found for other reasons to be unsatisfactory. Their resistance to abrasion is poor, while their expansion is about twice that of fireclay bricks. This causes the lining to exert a considerable pressure on the shell, and if for any reason it is found necessary to cool down the kiln, the bricks on cooling crack and fall out. They are better conductors of heat than firebricks, and cause a higher loss of heat by radiation from the shell. We have written of the kiln lining as being composed of bricks, but the practice is to use, in the clinkering zone and for some distance beyond, radial blocks of convenient size for handling, made to give a lining 9 inches thick. Beyond the blocks, ordinary 9-inch radial brickwork may be used.

When starting to use a new lining, it is necessary to coat its surface in the clinkering zone with a layer of molten clinker. The kiln is heated above the normal temperature, until the clinker is in a semi-molten state, which, as the kiln revolves, attaches itself to the lining. It is then cooled to the normal temperature, when the coating becomes pasty, and attaches to itself portions of clinker as the operation of burning continues. This coating, often some inches in thickness, protects the actual lining from extreme heat and abrasion, and materially lengthens the duration of its life. For this operation to be successful, it is necessary that the lining should not be either too soft or too hard. If too soft, a coating of suitable thickness will fall away, bringing portions of the lining with it; if too hard and smooth, the coating will not adhere.

Concrete composed of hard burned rotary kiln clinker and Portland cement has been used successfully as a lining. It is mixed in the proportion of 2 parts of clinker to 1 of slow-setting cement, with only sufficient water to cause the mixture to cohere when rammed into moulds. The blocks are allowed to harden for some time before use. They are also said to give good results when used in the clinkering zone of Schneider or Dietzsch kilns. This lining, while especially suitable for use in the clinkering zone, may be used with advantage in the whole length of a rotary kiln. In a new kiln, or in one being entirely relined, the lining may be done in situ when a reasonable time can be allowed for hardening before use. An inner shell of convenient length, and of 18 inches less diameter than the kiln, is adjusted within it at the upper end, and the concrete is rammed into the cavity. When this is sufficiently set, usually in about 24 hours, the shell is drawn forward and the operation is continued until the lining is complete, care being taken to maintain it of uniform thickness.

Concrete lining should be coated with clinker in the same manner as one of fireclay. With reasonable care a lining will last from 9 to 12 months in the clinkering zone and for some years above this zone.

**Clinker Coolers.**—In the early days of the rotary process, the clinker was allowed to fall from the kilns into heaps, which were raked down by hand labour, the hot clinker being cooled by simple exposure to the air. The difficulty of obtaining labour for this work, and its high cost in America, soon led to the introduction of mechanical appliances for cooling the clinker. One of the earliest of these was that of Messrs. Hurry and Seaman, used in connection with their type of kiln. The clinker is discharged from each kiln into a second cylinder, 30 feet long and 3 feet in diameter, lined with firebrick, and revolving about six times as fast as the kiln. Through these cylinders a current of air circulates which abstracts a portion of the heat from the clinker, and in its heated state forms the air supply to the kilns. The cylinders converge in pairs ; each pair discharges the now partially-cooled clinker into crushing rolls protected with casing. While passing through the rolls it is sprayed with water, and is discharged into a cylinder 60 feet long by 5 feet in diameter, lined with cast-iron plates, provided with ledges which lift and drop the clinker as it passes gradually through. A current of air circulating through the revolving cylinder completes the cooling process, and also draws off the steam from the rolls. The effect of spraying the clinker with water is to hydrate any uncombined lime present, thus avoiding the necessity of maturing the cement by storing. If properly managed, it in no way adversely affects either the grinding of the clinker or the quality of the resulting cement.

Vertical or tower coolers are sometimes employed, the hot clinker as discharged from the kiln being lifted into them by an elevator. They vary considerably in dimensions, in some cases one tower is provided for each kiln, in others one for each pair of kilns. Their internal construction varies, but the principle of their action is much the same in all. The inside of the tower is arranged with conical surfaces, over which the clinker spreads as it travels downwards, and is exposed to the action of cold air supplied through branches from a central blast pipe. Under one of these systems the clinker may also at the same time be sprayed with water.

By the regenerative system of Messrs. Lathbury and Spackman, the clinker is discharged into masonry vaults situated under the discharge hood of kilns. These vaults have sloping floors, outlets from which open into a tunnel. Cold air is forced into the lower level of the vaults, and, passing through the pile of hot clinker, becomes heated, when it is drawn off and forced back into the kilns, mixed with the pulverised coal. The same system is also sometimes carried out above ground in tanks built of steel plate, the clinker being lifted by an elevator. This arrangement is illustrated by Fig. 80, which represents one of the first rotary plants in Europe.
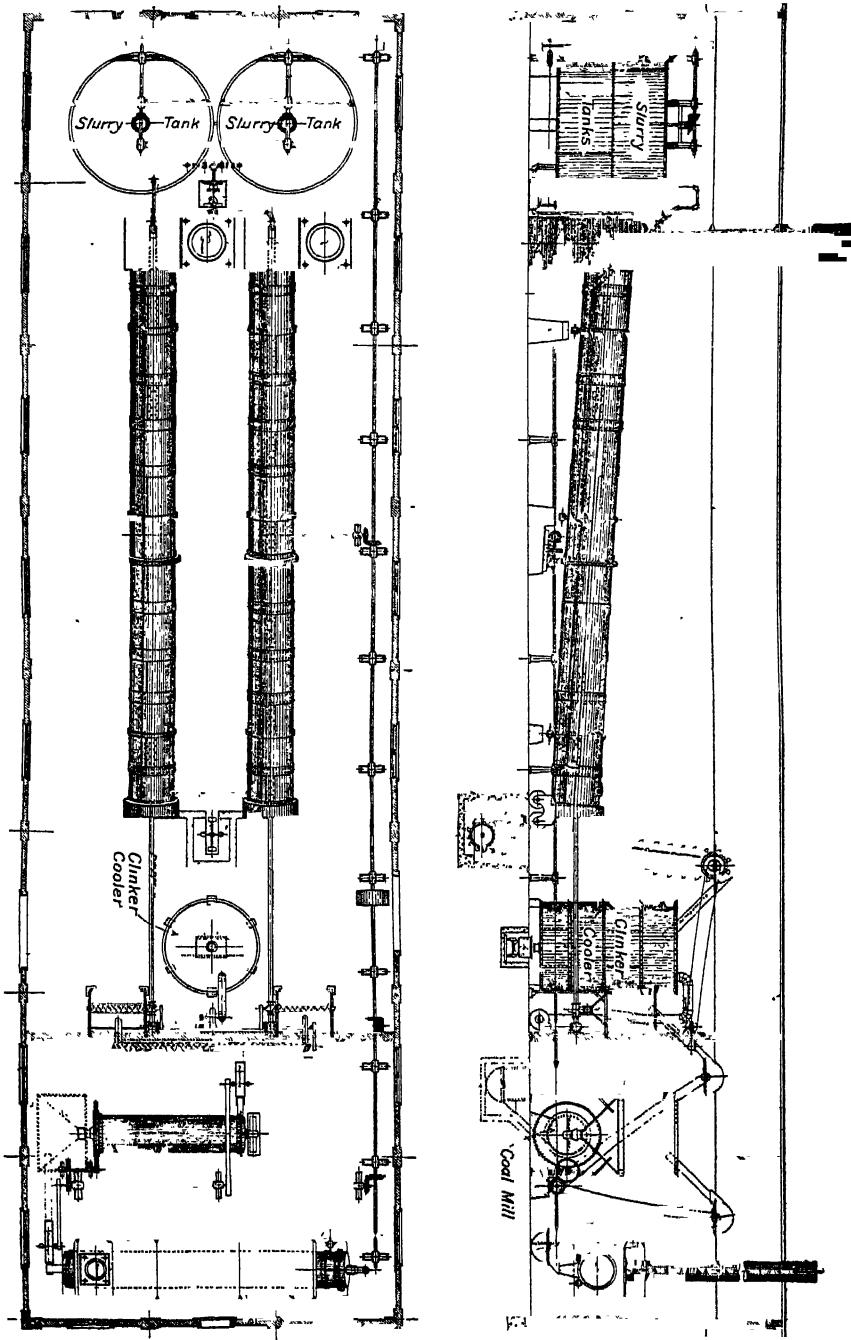
Fig. 80.—Plan and Side Elevation of a Pair of Rotary Kilns.

Shaking coolers, one being provided for each kiln, have been used. These are enclosed inclined trays kept in motion by cams attached to a revolving shaft. The hot clinker falls into them from the hood of the kilns ; it is then, by the jigging motion, spread over a series of shelves or steps, which form the bottom of the tray, and is gradually carried forward and discharged at the lower end. A large area of hot clinker is thus exposed to the action of the air, which is drawn in from both ends and discharged into a hot air chamber. From this chamber is taken the supply of air for the kilns ; the remainder passes away by a shaft.

The cooler now most frequently used, and solely used in Europe, is an inclined revolving cylinder arranged underneath each kiln. The hot clinker falls into it at the upper end from the hood, and during its passage downwards is exposed to a current of air drawn through by a fan. The heated air supplies that required by the kiln, into which it is delivered with the powdered coal, and is also used for heating the coal driers. Air from this source is sometimes used to heat the driers for raw materials, containing only a small quantity of moisture, when they are prepared by the dry process.

The rotary cooler is lined either entirely with firebrick, or partially so at its upper end, the remainder having a lining of cast-iron plates. Ledges, which may be formed by steel channels, are sometimes provided to lift and drop the clinker, so as to expose it effectually to the current of air. The dimensions of the cooler depend, of course, upon the output of the kiln, but it should be of sufficient capacity to cool the clinker to hand warmth. For kilns of from 150 to 200 feet long, the coolers are usually from 60 to 70 feet in length by from 6 to 7 feet in diameter. In some of the American works, early type kilns 60 or 70 feet long are quite successfully used as coolers for the longer modern ones.

**The Fuel for Rotary Kilns.**—We have seen that the producer-gas at first used in the Ransome and Stokes' kilns gave way in the early American experiments to the use of oil as fuel, this in its turn giving place to the employment of powdered coal. Oil is still in use to a limited extent in some American works, the consumption per barrel (375 lbs.) of cement being variously stated as from $9\frac{1}{2}$ to 14 gallons. It was, for a short time, in use at one of the Thames works. An analysis of the oil burned clinker is given in the table on p. 87 (No. 5). Natural gas, of which the principal constituent is methane or marsh gas, has been successfully used in the Kansas gas field, the volume required per barrel of cement being from 2,000 to 3,000 cubic feet. It is necessary to mix the correct volume of air required for complete combustion with the gas before admission to the kiln. This is 9·09 per cent. of gas to 90·91 of air by volume.

The opinion has been held that a sufficiently high temperature cannot be reached by the use of producer-gas without regeneration to calcine the Portland cement properly. As bearing on this, the results of the following experiment made in American works are of interest. Two rotary kilns,

60 feet long by 5 feet in diameter, were fired with powdered coal, and two with producer gas without regeneration. The raw material was slurry containing 60 per cent. of water; the experiments were conducted side by side and extended over a period of some months. In the coal-fired kilns the fuel consumption was 138 lbs. of coal per barrel of cement; in those fired with producer gas, 135 lbs. The result showed the efficiency of producer-gas, and apparently a small saving of fuel, but the producer involved the use of a better class of coal, and this was, consequently, more expensive, while the cost of labour for attending the producers was greater than that necessary when using powdered coal.

Bituminous coal has been found most suitable, anthracite being more difficult to ignite. The coal must be thoroughly dried before it can be ground, an operation requiring care to avoid loss of volatile constituents. Rotary driers, which have been described in Chapter V., generally heated by hot air from the clinker coolers, are employed for this purpose. The facility with which the coal is dried depends to some extent upon the constituents of the ash. Coal in which the ash is high in sand dries much more readily and completely than that in which it consists largely of clay.

The coal should be ground at least so finely as not to leave more than 25 per cent. of residue on a test sieve of 40,000 meshes to the square inch, but it cannot be too finely ground. The result of coarse grinding is an increased consumption. Many of the mills described in Chapter IX. are suitable for grinding coal, but whichever type is used should work free from escaping dust. The preliminary crushing is usually by roller or edge runner mills. In American practice, magnetic separators are sometimes employed at the crushing stage to remove "tramp" iron which might damage the mills. Tube mills are frequently used, either with a separate preliminary coarse grinder, or chambered, the coarse grinding chamber containing steel balls. Both the Griffin and the Fuller mills are largely used.

Powdered coal when diffused in air is highly explosive; it has been described as a tame variety of gunpowder. The coal mill should be kept well ventilated, and all conveyors and elevators should be entirely enclosed. Powdered coal is only stored in sufficient quantity to provide for the steady operation of the kilns, and generally also for the night shift. It is contained in specially constructed hoppers, in which it is kept in constant motion out of contact with air. If allowed to stand, it cakes and often inflames, and the finer it is ground the greater are these dangers. It is a good plan to keep a cylinder of liquid carbon dioxide in the coal mill in the event of fire occurring in the driers or grinding mills.

The Aero System.—By the " Aero System," which has been used to a limited extent in the United States, the coal is ground, without previous drying, in a high-speed centrifugal disintegrator. One machine is fixed in front of the discharge hood of each kiln, the action of the beaters providing

sufficient air, the supply of which can be regulated, for forcing the ground coal direct into the kiln. The disadvantages of the system are that the machine has to be placed very close to the hood, which somewhat inconveniences the burner in properly manipulating the kiln. Again, the coal cannot be so finely ground by this type of machine as by those previously mentioned, the result being an increased consumption. On the other hand, the cost of drying the coal is saved, while the plant itself is cheaper, being about one-third the cost of rotary driers and the ordinary type of grinding machinery.

**The Operation of the Kiln.**—For the successful operation of the rotary kiln, great skill and constant attention are required on the part of the burner, the raw mixture must be of accurate and uniform composition, and be uniformly and finely ground. The feed, both of raw material and air, must be constant and regular. The regulation of the draught is important, too little air results in incomplete combustion and a smoky fire, too much draught throws the clinkering zone farther back in the kiln and increases the temperature of the chimney gases, causing waste of fuel. A skilful burner can tell by the appearance of the flame whether the air supply is correct. As the raw material travels downwards in the kiln it gradually loses, in the first place water if present, then its carbon dioxide, until it reaches the clinkering zone, where it vitrifies, and is finally delivered at a temperature of about 1,350° C.

In order to throw some light on the changes that take place in the raw material as it travels through the kiln, the following experiment was made by W. B. Newberry.[*] A 60-feet kiln was cooled down without being emptied, samples being then taken at every 4 feet of its length and analysed, with the following results. The first sample was of unburned dry raw material as it entered the kiln, and the last was the finished clinker within 4 feet of the discharge at the lower end :—

| No. | $SiO_2$. | Fe and Al, | CaO. | MgO. | Loss on ignition. |
|---|---|---|---|---|---|
| 1 | 13·70 | 6·00 | 42·12 | 1·97 | 35·30 |
| 2 | 13·65 | 5·58 | 41·95 | 1·96 | 35·04 |
| 3 | 14·38 | 5·70 | 41·63 | 1·88 | 34·84 |
| 4 | 13·55 | 6·30 | 41·98 | 2·12 | 33·46 |
| 5 | 14·33 | 6·27 | 44·05 | 1·65 | 32·76 |
| 6 | 14·46 | 6·36 | 44·67 | 1·89 | 30·56 |
| 7 | 14·90 | 6·55 | 46·19 | 2·30 | 28·38 |
| 8 | 16·44 | 6·99 | 49·25 | 2·23 | 24·94 |
| 9 | 17·03 | 7·80 | 53·04 | 2·30 | 18·44 |
| 10 | 17·94 | 8·50 | 56·20 | 2·35 | 13·04 |
| 11 | 18·60 | 9·04 | 59·00 | 2·70 | 8·82 |
| 12 | 18·66 | 9·75 | 62·68 | 2·80 | 4·34 |
| 13 | 19·90 | 10·76 | 63·38 | 2·83 | 1·08 |
| 14 | 20·36 | 10·78 | 63·76 | 2·81 | ·86 |

[*] *Cement and Engineering News*, Chicago, vol. xii., 1902, p. 68.

" It will be seen from this that the process of burning in the rotary takes place not, as has been supposed, in a series of steps, but in a continuous progression, the moisture and organic matter beginning to pass off as soon as the raw material attains the temperature of the upper end of the rotary, shown by the change in colour from blue-grey to light buff or cream colour between 3 and 4. The carbonic acid soon follows, Nos. 4 and 5 at 16 and 20 feet showing marked loss. As the carbon dioxide burns off, the proportions of the solid elements rise steadily, the greatest variation being shown from 8 to 12, when the temperature passes from a bright red to a white heat. The whole of the volatile matter is, however, not driven off until the clinker is completely burned and about to leave the kiln, at which point but ·86 per cent. remains.

" Much of interest may be deduced from these results. The figures, however, tell their own story, and the limits of this article will not permit of more than a statement of the results of the experiment.

" The physical change from raw stone to clinker is shown by the characteristics of the different samples given below.

" Nos. 1, 2, and 3, blue-grey powder, changing to buff between 3 and 4.

" Nos. 4, 5, and 6, yellowish-buff powder, commencing in 6 to ball up into small lumps.

" Nos. 7, 8, 9, and 10, yellow to brown balls like marbles ; soft, easily crushed in the fingers, becoming darker and harder toward 10.

" No. 11, lumps quite hard and dark brown, traces of sintering on surface, softer inside.

" No. 12, lumps brown and partly sintered, beginning to lose regular rounded form, hard.

" No. 13, larger lumps, irregular and rough. almost black. Very noticeable difference between 12 and 13, latter is like brownish clinker and is burnt throughout.

" No. 14, smaller and more rounded lumps, black, has all the appearance of finished clinker ; in fact, no further change is seen as it leaves the rotary."

It would be interesting if a similar experiment was made on a modern long kiln. We are not aware if this has been done.

The coating of clinker on the lining has a tendency to increase in thickness, thereby reducing the sectional area of the clinkering zone. It sometimes occurs of fairly uniform thickness, but occasionally in irregular lumps, which rapidly increase in size, and adversely affect the efficient action of the kiln. If not removed at an early stage of formation they will probably fall away, bringing with them some of the true coating from the lining. If this happens soft clinker is beaten into the cavity with heavy bars, the patch being allowed to cool and harden before again starting work. The lumps should be dragged out and not allowed to travel down as the kiln rotates, as they would probably damage the lining. A frequent trouble is the

formation of rings of clinker entirely round the kiln, and these also must be removed.

It is usual to operate rotary kilns continuously—that is, 24 hours a day for 7 days a week—it being generally held that to avoid damage to the lining they should not be allowed to cool. The question of shutting down on Sundays was dealt with by W. S. Mallory, of the Edison Portland Cement Company, in a paper read at a meeting of the American Society of Portland Cement Manufacturers in December, 1910, from which what follows is an extract :—

" At the plant of the Edison Portland Cement Company for the past 18 weeks the entire plant, including the kilns, has ceased operations every Saturday at 6 p.m., and has resumed at 7 a.m., Monday morning, and there has been no trouble with the lining due to the fact that the kilns are stopped with the full load, and about every four hours from Saturday night until Monday morning each kiln is given a half-revolution, which transfers the heated material to the other side of the kiln lining, and so prevents it from cooling off too rapidly and becoming damaged. The increased output, I believe, is due to two reasons :—The men in charge of the kilns, on account of their rest, are in condition to do more efficient work, and because we further believe the output of our kilns depends on the area of the inside cross-section at its smallest point. When the kilns are down on Sunday, one gang of men, numbering from three to five, cut off the lining at its highest points and increase the area of cross-section, and the average output is increased. This operation cannot be done when the kilns are in continuous action.

" When the kilns are started on Monday morning, the heat is put on, but the kilns are not revolved until practically full heat has been obtained. In our case, it takes from $1\frac{1}{2}$ to 2 hours. By this means we do not get any underburned clinker mixed with the regular run of clinker.

" On Sundays we only employ 12 to 15 men, part of whom are watchmen, and the others we use on minor repairs, so as to have sufficient force in case of fire. Our power plant does not operate on Sundays. When the time comes for turning the kilns, one engineer who is on duty starts up an engine, and it is operated only long enough to turn each kiln one-half revolution, which does not take very long."

**Heat Losses—Regeneration.**—The heat losses of the rotary kiln are considerable, under the best conditions a very moderate quantity of the fuel consumed is actually used for calcination, the remainder being carried away as loss by radiation from the shell, by the clinker, and by the waste gases. The heat distribution has been frequently stated as approximately for calcination 20, loss by radiation 20, carried away by the gases 40, and by the clinker 20 per cent., but obviously the distribution will vary with the length of the kiln and the operating conditions. From the fuel point of

view, the rotary compares unfavourably with the continuous shaft kiln, but, on the other hand, the labour costs involved in briquetting the raw material, in charging, and in withdrawing the clinker from the latter kilns are avoided.

The quantity of heat radiated from the shell depends upon the thickness of the lining and coating, and the temperature of the escaping gases. As the lining burns away, the heat conducted to the shell increases with a consequent increasing loss by radiation. Some attention has been paid to the possibility of using an insulating material between the lining and the shell. R. K. Meade states that he has used asbestos millboard ¼ inch thick with good results, both protecting the tires and reducing the loss by radiation. An insulating material described as " Sil-o-cel," said to be made from celite, has been recently introduced in America, and is made in radiated brick form. The use of this would render necessary an increased diameter of the shell of the kiln at the clinkering zone.

We have, earlier in this chapter, dealt with the recovery and utilisation of heat from the cooling clinker.

The greatest loss is from the chimney gases, which, in the absence of induced mechanical draught capable of being regulated, must be maintained at a sufficiently high temperature to obtain sufficient draught. Much success has been achieved by employing them for raising steam in water-tube boilers, through which they are drawn by induced draught fans driven by variable-speed gear, and finally discharged into the chimney. The dust from the gases which is deposited on the tubes requires frequent removal. It is sometimes effected by the use of superheated steam.

**Comparative Merits of the Dry and the Slurry Process.**—At its inception, the rotary process was considered as only applicable to dry materials, and unsuitable for slurry. We have described how for the Stokes' process the slurry was dried by the waste gases from the kiln and broken up before burning ; while some American works using marl dried it in independently heated rotary driers. Newberry's experiments proved that either wet or dry material could be dealt with in the kiln, and the use of thick slurry prepared from soft materials became general, while hard materials continued to be treated by the dry process.

In Chapter XI. the preparation of thick slurry has been described. For calcination in the rotary kiln it may contain from 35 to 45 per cent. of water, this depending on the nature of the materials from which it is prepared. Slurry from soft materials to be of equal consistency with that from hard will contain more water.

It is now quite common practice to treat even hard materials by the slurry process, rather than by the dry, and each has its advocates. With soft easily reduced materials, such as chalk, marls, and clay, which carry a considerable quantity of water, there can be no question that the slurry

process is most suitable. Still, there are instances in which such materials are treated in the dry way. For hard materials the choice must depend on their nature and chemical composition.

Hard clean limestone approximating in chemical composition to a cement mixture, the small quantity of moisture present in which is easily removed before grinding, may certainly be most economically treated in the dry way, while for stone of irregular composition, especially if it has adhering shale or clay, the slurry process is perhaps most suitable, but still much of such material is treated by the dry method. Both methods are in use in England for dealing with the materials of the lias formation.

The capital cost of a wet process plant is less than that of a dry one, it is simpler and its upkeep is less. It requires less power, and there is an entire absence of dust in the raw department of the works. No preliminary drying of the raw materials is necessary. The water is driven off in the first 40 feet of the kiln, which for slurry should be longer than for dry flour. With suitably designed plant equally good cement may be made by either method.

**Separation of Dust and Recovery of Potash from the Kiln Gases.**—During the early years of the rotary process little or no attention was paid to the dust carried out of the kilns by the waste gases, which escaped from the chimneys, and was not only itself a loss, but was a cause of frequent trouble to the country surrounding the works. Various methods for arresting it were devised ; these generally consisted of chambers with baffle walls situated between the end of the kiln and the chimney, in which the gases expanded, their velocity being consequently reduced. The effect of the reduced velocity was to cause a deposit of dust, which settled on the floors of the chambers, from which it was withdrawn by worm conveyors and returned to the kilns. Although much was recovered in this way, the method was not completely effective.

The first attempt to deal efficiently with the dust problem was made in Southern California. Growers of oranges asserted that dust from the cement works at Colton and Riverside was injurious to the groves, and they obtained injunctions against the proprietors of these works, by which they were compelled either to shut down altogether or to prevent effectually the escape of dust. This led to the adoption of expansion chambers at Colton, and the electrical precipitation process of Dr. F. G. Cottrell at Riverside. By this process, discharges of high tension direct current are produced from electrodes arranged in a chamber through which the dust-laden gases pass. The dust particles move, with a velocity proportional to their charge, towards the electrodes of opposite sign, which are arranged as a surface upon which the particles are precipitated, and from which they are removed at stated periods by shaking, while the gases are diverted to another chamber.

The dearth of potash during the late war rendered it necessary to seek

new sources of supply, and the possibility of obtaining it from the dust and gases of rotary cement kilns received considerable attention. The fact that it was practicable to recover potash as a by-product in the Portland cement industry was, we believe, first pointed out by Dr. Clifford Richardson in the course of a meeting at Atlantic City in June, 1904, but it was not until the outbreak of war that the matter received practical attention.

All cement raw mixtures contain potash in small quantity combined as silicate. In some of the analyses, of which the results are given in Chapter VIII., figures are stated. The United States Department of Agriculture obtained samples of the raw mixture from 113 American cement plants in which the potash was determined. It was found to vary from ·2 to 1·16 per cent. Heated to high temperatures, even to fusion, a potash silicate such as felspar is not decomposed, but in the presence of lime a double silicate of calcium and aluminium is formed, and the potash is partially set free and volatilised, the quantity depending on the amount of lime present, the temperature of ignition and its duration. From a cement mixture about 60 per cent. of that present may be obtained. It has been proposed to include felspar in the raw mixture to obtain a higher yield, and with an aluminous mixture this would be quite feasible and indeed an advantage, as it would increase the content of silica.

The first plant installed for the recovery of potash was at Security in Maryland, those in California originally being only intended for the precipitation of dust. Both plants now recover the potash. Much pioneer work was done at Security by Mr. J. J. Porter. At Riverside the collecting electrodes or " treaters " were suspended angle iron frames on which heavy woven wire was stretched. At Security the pipe form was introduced, and this is now generally employed. Each unit consists of a sheet steel pipe about 12 inches in diameter and 18 feet long suspended vertically, the number in one chamber being from 80 to 240. The arrangement seems somewhat similar to that of a Green's economiser. The discharge electrode is a wire suspended in the centre of each pipe, the walls of the pipe form the collecting electrode. At stated intervals the gases are diverted and the pipes are cleaned by shaking, as is done with the flat treaters at Riverside.

Although the quantity of potash obtainable as a by-product of the cement industry is small, its recovery during the closing years of the war was found to be profitable. In 1917, Mr. Porter stated that the recovery of potash at Security had already more than paid the cost of installation of the plant, and the results indicated that it would be possible to compete with German potash on a pre-war basis, and still make a fair profit. From a publication issued by the United States Geological Survey, it appears that at the end of 1918, 11 plants were working in the States—viz., 3 in California, 1 in Indiana, 1 in Maryland, 1 in New York, 3 in Pennsylvania, and 2 in Utah— while 4 more were reported as under construction.

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At the Dalen Portland Cement Works at Dalen, in Norway, 30 tons of dust are obtained daily by electrical precipitation. The potash is not extracted, but the dust is collected in bins, from which it is sacked up and sold as a fertiliser.

The whole of the volatilised potash is not removed from the gases by the precipitation of the dust. To obtain this, they are, after depositing the heavier dust, passed into a second treater in which water circulates in a thin film over the collecting electrodes until it is saturated with potash; this process also thoroughly cleans the gases from the dust not precipitated in the dry treater. The potash in the solid matter separated from the gases occurs in three forms, that insoluble, this being contained in the undecomposed raw material of which the dust largely consists, that freely soluble in water, and that slowly soluble. In the last-named form it may be brought into solution by boiling with water for 10 hours, by digesting with water at 100 lbs. pressure for one hour, or by heating with very dilute acids. It is supposed to be formed by re-combination of the volatilised potash with the silicates of the fuel ash. The slowly soluble form does not occur, or exists only in small quantity, when oil is used as fuel, as it is at Riverside.

Based on his experience and experiments, Mr. Porter suggests the following as the ideal procedure in the collection of potash :—*

"First pass the gases at a relative velocity through a preliminary dry precipitator. The purpose of this would be to take out from 50 to 75 per cent. of the coarsest dust, which should then be returned to the kilns. With this dust would also be taken out a certain proportion of the potash, but this proportion would be small relative to the dust, and would not be entirely lost, as it would pass again through the kilns.

"The gases should next pass through a water film treater, where the balance of the dust and practically all of the potash would be collected. The solution obtained here would be circulated through the water film treater until nearly saturated with potash salts, and would then be evaporated, by the waste heat of the gases, for the recovery of these salts. The sludge containing the insoluble material would be treated in digesters at 100 lbs. pressure for one hour, in order to liberate the recombined potash. It would then be filter-pressed, and the solution containing the potash would be combined with the original solution and evaporated. The filter-press cake would be returned to the kilns."

**Portland Cement manufactured from Fused Clinker.**—It has been frequently maintained by cement experts that, in order to produce perfect Portland cement, the raw materials must be raised to the temperature of incipient fusion, but that it was fatal to exceed this temperature and to fuse any considerable portion of the mass. Indeed, in many works the acci-

* From a paper presented before the Portland Cement Association, Chicago, September 10th to 13th, 1917.

dentally vitrified clinker has been picked out and rejected. This opinion has been traversed by Bertram Blount, who asserts with great show of reason that by suitably proportioning the constituents they may without other preparation be tipped into a furnace and withdrawn as molten slag. He holds that the resulting product would be superior to that obtained in the ordinary way in a cement kiln—Dr. Michaelis in Germany held a similar view. We believe that some experiments were at one time made at the Atlas Cement Work in Pennsylvania, but we do not know the result. The process is one that we think might easily be experimented with in a foundry cupola, but it would perhaps be advisable in its initial stages to work with a mixture prepared in the ordinary way and briquetted. Alumina cements are now being made in France from molten ingredients in electric furnaces. Cements of this kind set quickly and attain great strength in a few hours.

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# CHAPTER XV.

## GRINDING, STORING, AND PACKING CEMENT.

CONTENTS.—Process of Grinding—The Hardness of Clinker—Regulating the Setting Time of Cement during Grinding—Storing Clinker—Fineness of Grinding—Storing and Packing Cement—Clearing House for Bags in Westphalia.

**Process of Grinding.**—In Chapter IX. the most important types of grinding machinery have been described. The general trend of modern practice is in the direction of grinding by successive stages or gradual reduction, it having been found unsatisfactory to attempt to attain the fineness now required by single-stage grinding. This can, however, be done by some of the mills we have described, but with a reduced output. The Fuller and the Griffin mills can be made to yield a sufficiently fine product by fitting them with suitable sieves ; the Fuller is also frequently used as a pre-grinder for tube mills. As we have seen, both the Sturtevant and the Kent mills yield a product containing a large per cent. of sufficiently fine matter mixed with coarse grit, which is separated and returned to the mill. Stage grinding in a single machine is possible in the compound mill, commencing in the first chamber with steel balls, followed by pebbles, with a final chamber containing cylpebs or other bodies adapted for fine grinding. But when finishing with the tube mill, the pre-grinding is best done on a separate machine.

The efficiency of the tube mill depends on the fineness of the material with which it is fed, and in this connection the following quite recently obtained results are of interest. At the Coplay Cement Works, in Pennsylvania, a 57-inch Fuller mill was grinding cement clinker for finishing in tube mills, the fineness of the finished cement being 80 per cent., passing a sieve of 200 meshes to the lineal inch. The mill required 150 H.P. to produce from 20 to 25 barrels per hour—a very poor result for such an expenditure of power. As will be seen by referring to Fig. 28, Chapter IX., the mill contains 4 balls and 4 pushers. As an experiment two of the balls and pushers were taken out and replaced by ploughs. One result of this was that the power was reduced, and the mill now absorbed only from 65 to 70 H.P. But it was also found that the output was increased to from 60 to 75 barrels per hour of finer material, while that from the tube mills was now so fine that 90 per cent. passed the 200 sieve. The effect of the ploughs

was to keep the material in a state of agitation, thus facilitating its removal from the mill as fast as ground, whereby a supply of unground material in advance of the oncoming balls was maintained.

Clinker burned in any type of fixed kiln is always more easy to grind than that from the rotary kiln. Assuming it to be sufficiently burned, the facility with which it can be ground depends largely upon the composition of the raw materials, the proportions in which they are mixed, and the care bestowed upon their preparation. A high ratio of silica to alumina, together with the highest proportion of lime that can be safely carried, the mixture being carefully prepared, results in clinker that grinds freely. On the other hand, a low lime, high alumina mixture, produces dense vitrified clinker most difficult to grind.

Although the clinker is usually taken direct from the kilns to the mills, it is sometimes stored in bulk under sheds, with the object of rendering it more easily ground. This is certainly the case with fixed kiln clinker, which largely disintegrates after a few weeks' storage, especially if watered slightly as taken from the kilns. This treatment tends to improve the soundness of the cement, but rotary clinker undergoes little change, either as regards easier grinding or improved soundness, even after prolonged storage.

Theoretically, cement should be so manufactured as to be constant in volume and in soundness, when ground from clinker straight from the kilns, but practically this is not always the case. The effect of grinding with a little moisture will render it sound, either immediately, or after storing in bulk. A process devised by H. K. G. Bamber * effects immediate hydration of the unsound particles, and is applied to grinding in tube mills. The feed worm is arranged on a tubular shaft, through which steam at a temperature of from 100° to 150° C. is continuously admitted to the interior of the mill. Every particle of the cement as it is broken up and travels onwards comes into contact with the heated moist atmosphere, and perfect hydration of any portion that would cause unsoundness takes place. Cement after treatment in this manner becomes perfectly sound, and will conform to any recognised accelerated test immediately on leaving the mill. The process is in no way detrimental and, contrary to what might be expected, the quantity of water absorbed by the cement is small, rarely reaching 2 per cent. with well burned clinker.

During grinding, measures must, if necessary, be taken to regulate the setting time of the cement. This is effected by the careful addition of a small quantity of gypsum, by an automatic arrangement, during the first stage of grinding, to ensure a proper mixture. The amount varies with the rate of setting required. Fixed kiln clinker frequently does not require this addition, but cement from rotary clinker if untreated will set instantaneously.

* *Proceedings Inst. C.E.*, vol. clxxxiii., part 1.

Most specifications fix a maximum permissible limit for sulphuric acid ($SO^3$). In the British Standard Specification this is 2·75 per cent.

**Fineness of Grinding.**—From an early period in its history there has been a gradual but continuous improvement in the fineness of Portland cement, and, at the same time, an increasing demand for cement of greater strength, which could only be reached by more highly limed and heavily burned clinker most difficult to grind. From some notes made in 1879, we give the fineness of ordinary commercial cement of that date. It was ground by millstones from hard well-burned clinker, and was not sifted.

On test sieve having 30 meshes to the lineal inch,   .   10 per cent. of residue.
   ,,      ,,    40     ,,       ,,      . 25·6    ,.     ,,
   ,,      ,,    50     ,,       ,,      . 31·8    ,,     ,,
   ,,      ,,   100     ,,       ,,      . 44·4    ,,     ,,

This cement, as regards fineness, was fairly representative of much of that on the English market at that time ; to-day it would be considered as only suitable for feeding tube mills. Cement leaving from 5 to 10 per cent. of residue on a sieve of 50 meshes to the lineal inch could be obtained if specified, this fineness was generally accepted as a standard, and was usually obtained by careful milling without sifting. About the year 1878, the use of sieves, and later the air separator, became general in English cement works.

Coarse as we now consider such cement to have been, good work was done with it, much of which will be found recorded in the *Proceedings of the Institution of Civil Engineers*, as also results of experiments extending over long periods of time. Constancy of volume or soundness tests, which have only during recent years become general, are in many cases not referred to, but it may be fairly assumed that cement which continued to increase in strength with the lapse of time must have been sound and good at the commencement, although coarsely ground.

The effect of grinding is to render the clinker chemically active and capable of combining with water to form a hydrate, but only the impalpable portion of the cement, that too fine to ·be retained on any sieve however fine, exists in the active state. If a sample of cement is ground so finely as entirely to pass through a sieve of 180 meshes to the lineal inch and then through one of 200 meshes—which are those now generally in use for testing fineness—the residues obtained on the latter will be found to possess little if any setting or hardening properties. Much experimental work has been done in testing the comparative values of coarse and finely ground cement, and it is now generally admitted that, as regards capacity for admixture with sand, finely ground cement gives the best results. The effect of fine grinding is to increase the rapidity of setting and, in the early stages, also the hardening, as compared with cement more coarsely ground.

Some comparative experiments to test the value of fine grinding were recently made by the United States Bureau of Standards with ordinary commercial cement, and the same cement ground 12 per cent. finer. In concrete mixtures, with various proportions of aggregate made with each cement, it was found that those made with the fine cement were invariably the strongest. The average increased strength of the fine cement concrete compared with that from the ordinary cement was 66 per cent. at seven days and 42 per cent. after six months, and was greater in the richer mixtures. In 1 to 3 sand mortar, the fine cement gave a greater increase than when used in 1 to 3 concrete.

The following table gives the quantity of aggregate that might have been used in actual work with each cement in various proportions to give concrete of equal strength after 28 days' hardening, and the weight of cement saved :—

| With Ordinary Cement. | With Fine Cement. | Cement Saved per cubic yard. |
|---|---|---|
| 1 to 3½ | 1 to 5 | 197·4 lbs. |
| 1 to 4½ | 1 to 6 | 141·0 lbs. |
| 1 to 6 | 1 to 8 | 76·8 lbs. |

**Result of the Deficiency of Impalpable Material in Cement.**—This result is shown by the following description of an attempt to grind by a system of gradual reduction with rollers which was made by Dr. Tomei at the Quistorp Cement Works, in Germany, in 1880. The mills, with steel rollers, were specially constructed for grinding cement. The rollers were most accurately turned and polished, and were set so closely together that a sheet of note-paper when passed through them was marked equally on both sides. Their total width was 19 inches, and they were driven at differential speeds to attain a certain amount of rubbing action. Two pairs of freshly dressed millstones 4 feet 3 inches in diameter, and running at from 110 to 115 revolutions per minute, yielded on the average of a nine hours' test 8·5 tons of cement per hour, ground so finely that the residue on a sieve with 5,896 meshes to the square inch was 16 per cent.

Twenty-three horse-power was indicated by careful brake experiments, and the temperature of the product leaving the mills was 86°. The output seems high, especially as the speed of the stones was low. Stones of this diameter might have been safely driven at 150 revolutions. Exactly the same amount of power sufficed in the parallel experiment to drive two sets of rolls and one pair of similar stones. The yield from this combination was 14·5 tons per hour with a 13 per cent. residue on the sieve of 5,806 meshes per square inch.

In order to test the comparative strength, samples of the material produced in either way were carefully checked by the sieve and made into briquettes, neat and with standard sand.

The cement from the stones left a residue on the sieve with 5,806 meshes to the square inch of 15·74 per cent., and on a sieve with 32,275 meshes to the inch of 21·15 per cent. ; the total of the coarse particles from both sieves being thus 36·189 per cent. The following table shows the tensile strength of the cement in lbs. per square inch, neat and with 3 parts of standard sand :—

|  | 7 days. | 28 days. |
|---|---|---|
| Neat, . . . . . . | 428·1 | 480·7 |
| 1 to 3 sand, . . . . . | 173·5 | 240·1 |

A sample of exactly the same cement produced by the roller mill left a residue on the 5,806-mesh sieve of 13·63 per cent., and on the 32,275-mesh of 23·44 per cent. The tensile strength tested as before was as follows :—

|  | 7 days. | 28 days. |
|---|---|---|
| Neat, . . . . . . | 378·4 | 492·3 |
| 1 to 3 sand, . . . . . | 163·6 | 251·8 |

It appears from the figures that, though the results were a little in favour of the stones at seven.days, the twenty-eight days' test gives the advantage to the rollers, and we take it that, so far as the quality of the cement is concerned, there was practically no difference whatever in the two products.

These tests certainly explain the reasons for the confidence, at one time expressed by foreign manufacturers, in the roller mills, but a plant erected at great cost by a firm of cement manufacturers on the Medway proved a complete failure. It ground the cement to the required fineness when tested on the sieves of 50 and 80 meshes to the lineal inch, which were those generally employed at that time for testing fineness, but the difference in the comparative strength of cement prepared by millstones alone in the ordinary way and that when done by the roller plant was most apparent, it was fully one-third less for the roller-ground, when tested neat, and the difference was still greater when tested with standard sand. The setting was always slow, even with an otherwise quick-setting sample. When tested by sifting through fine silk sieves, the cause of failure was revealed. It was found to be the deficiency of impalpable powder in the roller-ground cement, when compared with that ground by millstones. Later, it was discovered that it was the practice in German works using roller mills to mix in one conveyor the product from the rollers and stones, and so the fault had not made itself apparent. Methods for determining the impalpable powder in cement will be described in the chapter on cement testing.

**Effect of Fine Grinding on Soundness.**—An argument which has been advanced is that cement, which if it was coarsely ground would be unsound and unsafe to use, is by fine grinding rendered perfectly sound and good, and this is in many cases undoubtedly true. Unsoundness may result from either incorrect proportions, coarse·grinding, and irregular mixtures of the

raw materials, or from all of these causes. The resulting clinker in such cases will consist, not only of the true cement compounds, but also of un-combined or imperfectly combined lime. Upon the addition of water to the resulting mortar, the fine particles are immediately acted upon and become hydrated, the coarser ones may be acted upon after a long period of time, the result being ultimately the complete disintegration of the mass. If the cement is brought into an extremely fine state of division, the un-combined lime may be hydrated and rendered harmless before setting takes place, especially if this occurs slowly.

**Replacement of the Coarse Particles by Sand, Defective Sand.**—It has been stated that the coarse particles that may be separated from cement by sieves are not more efficient than sand, and that the cement would be of equal value if they were removed and replaced by sand. It will be inferred from what we have just said respecting unsound cement that this may be true, or partially true ; indeed, it would probably very much improve it. But, with such a replacement in a sound cement, there would certainly be a decrease in strength, for there is undoubtedly some contact action between the coarse particles and the impalpable powder which facilitates the hardening.

The proposition is not a practical one, but, to ascertain the effect of replacing a portion of the residue or core by sand, we made the following experiment with a sound cement :—

The sample was sifted through a sieve having 100 meshes to the lineal inch, the residue was graded with coarser sieves and the fractions weighed. Coarse clean Leighton Buzzard sand was ground in the same mill as the cement, and to a similar fineness. This was sifted through the 100-mesh sieve and the residue separated into fractions similar to those obtained from the cement. Quantities equal in weight to those of the fractions removed were added to the sifted cement, the whole thoroughly mixed and the mixture tested, with the result that the strength was far below that of the original cement.

As the fineness of cement increased it became generally known that in use it would bear the admixture of more sand. The proportion of sand may really be adjusted to the fineness of the cement. If the sand is of good quality, as is usually the case on large and properly supervised works, a less proportion of fine cement than of coarse may be used to an equal quantity of sand with equally good results as regards the quality of the work produced and at a less cost. Large quantities of cement are, however, not used under such favourable conditions, and much of the sand employed is of very in-ferior quality, scarcely deserving the name of sand. A growing tendency exists to use increased quantities of sand, no matter what its quality may be, with the result that much inferior work is being done with very good cement.

**Storing and Packing.**—From the grinding mills the cement is transmitted by elevators and worm or belt conveyors to the storage bins or silos. These are generally entirely closed up while being filled, the conveyor discharging at the top, the cement thus being distributed layer above layer. It may be automatically weighed at any convenient spot on its way to the silos, the machine recording the quantity which has passed through it. In this country the usual practice is to fill and weigh the casks or sacks by hand, the floor of the store or silo being on a level with the loading platform. In some Continental works the silos form an upper storey, the bottoms of the silos being hoppered and brought down to spouts, which discharge into casks or sacks on a floor at the loading level.

In many American works the packing is entirely distinct from the storage department. The bins or silos are arranged on the ground level in such a manner that they be made to discharge their contents automatically into a tunnel common to all. A screw-conveyor running through this tunnel conducts the cement to the packing room, where it is lifted by an elevator to a hopper, from which it is drawn by spouts. Both in Continental and American works, but especially in the latter, owing to the high cost of labour, the packing is frequently done by machine, for which purpose it is necessary that the cement should be drawn from silos or from a hopper placed overhead.

For casks it is convenient to employ a machine, which not only delivers the cement into the casks, but also, by means of a mechanical arrangement, provides that every cask shall be shaken during the filling process, so as to secure uniformity of loading. It is also possible to connect such filling machines with a standard weighing machine which cuts off the supply of cement automatically as soon as the cask has received its full charge. To prevent the escape of dust the cask is covered with a hood which can easily be adjusted by hand. By means of branched spouts it is possible to arrange for the filling of two or more casks simultaneously, all the casks being placed upon a rocking platform to shake down the contents uniformly. An apparatus precisely on the same principle has been arranged for filling bags and for weighing the contents, the supply, as in the case of casks, being automatically cut off.

**The Exilor.**—This machine for filling sacks is the invention of Messrs. F. L. Smidth & Co. It is illustrated by Fig. 81. It consists of two similar air-tight chambers placed side by side, one door hinged between them closing either chamber. By means of a small vacuum pump, air may be exhausted from either of them. A pipe which terminates in two branches, one entering each chamber, is inserted into the bulk of the cement in the bin or silo. The sack, into the mouth of which the tube enters, is hung at the end of a scale beam, at the other end of which is a pan and weight that will exactly balance a filled sack. On closing the door the exhaust commences, and a

stream of cement is drawn into the sack. When the required weight is reached, the beam falls, and by falling opens an air valve that breaks the vacuum and stops the flow of cement. The door is opened and closed on the



Fig. 81.—The Exilor for Packing Cement.

adjoining chamber, from which a filled sack has been removed and replaced by an empty one. The process is thus continuous from one chamber to the

other alternately.   The operation is dustless ;   on opening the door to remove the filled sack a small fan is set in motion, which withdraws the dust to a dust filter.   It is stated that three men will fill, and wheel away, 150 sacks per hour.   The machine has been adapted for filling casks, and shaking them while filling.

**Packages.**—The use of casks for the home trade has gradually fallen into almost entire disuse, but they are still largely employed for the export of cement.   The standard is 28½ inches high with a diameter of 16 inches over the head.   They are made of fir, the staves in the best English and German practice being grooved and tongued, and are bound with either hazel or Dutch hoops and two or four iron hoops.   The " barrel " is still often referred to as the unit of weight of cement, especially in America.   It contains 376 lbs. of cement.

For the home trade, bags of jute cloth which will contain either 200 or 212 lbs. of cement are used.   They are branded, and returnable to the factory, where they are cleaned, repaired, and used again as long as serviceable.

**Clearing House for Returned Bags.**—The department dealing with returned bags in a cement manufactory is a troublesome one, involving much detail work.   Friction is frequently caused by a purchaser sending bags to one maker bearing another maker's brand, and expecting credit for them. The Rhenish Westphalia Cement Syndicate has a system of dealing with returned bags which, although not applicable in this country, is worthy of notice.   It is a large syndicate having had in January, 1914, when a new agreement was entered into, 35 members with a yearly output of 2,098,400 barrels.   It has a clearing house in Munster, to which all bags originally sent by any member of the syndicate are returned.   After examination for strangers and those so badly damaged as to be of no further use, credit is given to the sender.   The bags are dried if necessary, cleaned, repaired, sorted, and finally baled up and sent in full truck loads to the place of origin.

# CHAPTER XVI.

## CEMENT TESTING.

**Early Cement Tests.**—The makers of the quick-setting cement of the Roman cement type were fond of displaying the tenacity and tensile strength of that material by the construction of horizontal beams of brickwork, which were built out from a wall a brick at a time. Sometimes a whole day was allowed to elapse between the placing of each brick; at others the fresh bricks were added as soon as the last made joint had become set. For this purpose some five or six minutes would suffice with the best quality of Sheppey cement, and General Pasley observes: "It was stated in my presence at one of the meetings of the Institution of Civil Engineers, by members of that Society, that so many as thirty bricks had been stuck out in one day, and thirty-three bricks in thirty-three days in the same manner." Messrs. Francis had similar beams at their works, and General Pasley tested his artificial cement both by building out the beams with the bricks laid horizontally, and also with the bricks arranged in a vertical position, in which latter case a far greater number could be supported.

**Doubtful Value of these Tests.**—He says, when speaking of this system of testing: "Considering that this mode of setting out bricks from a wall, though an excellent test of the quality of different sorts of cement, if always done under the like circumstances, might be supposed doubtful, if executed by workmen of unequal skill, or not precisely in the same manner, and in different states of weather or of temperature; and considering also that a pier (beam) of this sort, exhibited at the premises of any cement manufacturer, might not be considered satisfactory by persons who had not been actually present at the time the bricks were placed; since there can be no doubt that, by permanently supporting such piers for several months, a much greater effect would be produced than by the mode I have described of only holding each successive brick a few minutes by a trowel; it therefore appeared

desirable when we first prepared for commencing those experimental piers (beams), to make arrangements also for trying the comparative strength of the same from artificial mixtures by tearing them gradually to pieces by a dead weight."

**General Pasley's Tests.**—He then describes a plan of uniting three (afterwards four) bricks together on the flat by two joints of 9 inches by 4½ inches, having mortises cut in the upper and lower bricks for receiving iron nippers. After allowing from thirty-six to forty-three days for the induration of the cement, the joints were torn asunder by gradually applied weights, laid on by ½ cwt. at a time, in an apparatus which was in the nature of a gigantic scale-pan. It was found that when only three bricks were used the weight generally fractured the uppermost bricks by tearing them apart at the mortises, so that in the later experiments four bricks were used, and the mortises were cut in the top and bottom bricks, by which means the solid part above and below the mortises is strengthened by the thickness of one entire brick and a cement joint, leaving the centre joint only exposed to the full action of the breaking apparatus.
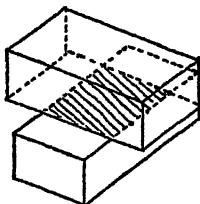


Fig. 82.—Bricks joined crosswise for Cement Testing.

**Unscientific Nature of the Early Cement Tests.**—All of these tests, and even those obtained in later times by joining two bricks together crosswise, so as to obtain a cement or mortar joint 4½ inches by 4½ inches = 20¼ square inches in area (see Fig. 82), were far from scientific, and it was not until recent times that the more accurate and reliable system of using briquettes, having a standard area at the neck or point selected for fracture, came into use. These notched briquettes appear to have been first used by French engineers. For an early test of Portland cement briquettes of this kind, see the experiments at the 1851 Exhibition, p. 44.

**The Value of Portland Cement made known by Testing.**—The estimation in which Portland cement is at present held, the reputation it enjoys among engineers, and indeed its high position as a building material are mainly due to the tests it has undergone in the past, and to its behaviour under others of like character and of increasing severity that are constantly being applied to it. It was pointed out many years ago at the Institution of Civil Engineers that, in introducing a cement of this nature, it was very necessary

to adopt some general standard of excellence, and the first record we can find of any systematic experiments with Portland cement were those conducted by the Ingénieurs des Ponts et Chaussées, by whom this material was employed on a large scale about 1848 to 1850.

**Early French Tests of Portland Cement.**—The French tests in use at that period were in the main as follows :—

Specific weight 1,200 kilogrammes per cubic metre, or 96 lbs. per imperial bushel. Tensile strength of briquettes on the area of 2·25 square inches.

| | Neat Cement. Kilogrammes. | | Lbs. | 1 Cement to 2 parts Sand. Kilogrammes. | | Lbs. |
|---|---|---|---|---|---|---|
| In 2 days, . | . 64 | = | 141 | .. | | .. |
| „ 5 „ . | . 128 | = | 282 | 64 | = | 141 |
| „ 30 „ . | . 240 | = | 529 | 128 | = | 282 |

**Tests by Mr. Druce and Mr. Rendel.**—Very shortly after this date Portland cement was used extensively on English harbour works by Mr. Rendel and by Mr. Druce at Holyhead and Dover, and these gentlemen subjected the material to searching tests, but it does not appear that its compliance with any definite standard was at that time insisted upon.

**Mr. John Grant's Tests.**—The engineers of the Metropolitan Board of Works were the first public officials in this country to institute analogous tests to those adopted in France, and to the late Mr. John Grant, M.Inst.C.E., who was mainly responsible for these tests, and who on several occasions presented to the public the results of the long and laborious investigations carried out by him respecting the strength of Portland cement, we are largely indebted for our present knowledge of the properties of this material, and for the vast improvements which manufacturers have been able to effect in its quality of late years.

**Mr. Grant's Essay on Cement in 1865.**—In a paper entitled "Experiments on the strength of cement," communicated to the Institution of Civil Engineers in December, 1865, Mr. Grant described the steps taken by him during the construction of the southern portion of the Metropolitan Main Drainage Works, in order to ensure the use of cement of the best quality only. He points out that previous to 1859 Roman cement was with but few exceptions employed for the inverts of the London sewers, the arches being set in blue lias lime, and Portland cement being "scarcely ever tried." It was, in fact, until this time chiefly employed as a stucco, and in ordinary building operations, though it had been, as we have seen, used at Dover and elsewhere mainly for the formation of concrete blocks, and it had already been largely adopted abroad.

**Mr. Grant's First Specification Based on Tests.**—After some preliminary tests with samples of cement procured for the purpose from various

manufacturers, and some corresponding trials of cement obtained from the makers in the ordinary way, the following clause was inserted in the specification for the Southern high-level sewer, dated 1859, being the first contract under the Metropolitan Board of Works on the south side of the River Thames :—

"The whole of the cement to be used in these works, and referred to in this specification, is to be Portland cement, of the very best quality, ground extremely fine, weighing not less than 110 lbs. to the striked bushel, and capable of maintaining a breaking weight of 400 lbs. on an area 1½ inches by 1½ inches, equal to 2¼ square inches, seven days after being made in an iron mould of the form and dimensions shown on drawing (Fig. 83), and immersed six of these days in water."

**Mould for Forming Briquettes for Testing.**— In order to prepare the requisite test-briquettes, a moulding machine of simple construction was introduced, and bell-metal moulds, having a sectional area of 1½ inches by 1½ inches at the breaking point, were employed. The moulds were originally provided with linings or templates of thin iron, which exactly fitted them and enabled the briquettes to be removed directly they were formed. The moulding apparatus, as also the testing machine, were made by Mr. P. Adie, and these appliances were speedily adopted by all cement manufacturers as well as by most large users of cement, while this system of testing soon became the recognised plan of judging the quality of cement throughout the country.



Fig. 83.—Mr. Grant's Original Test Briquette.

**Tests made by Ordinary Workmen.**— No difficulty was experienced in training an ordinary workman to carry out these tests, and the process was found to answer well in the case of 70,000 tons of Portland cement used during the construction of the first portion of the outfall works.

**Objections to Severity of Test by Manufacturers of Cement.**—It seems now somewhat strange to read that in the first instance objection was taken by manufacturers to the standard then proposed of 400 lbs. tensile strength to the 2¼ square inches, and it was urged that 300 lbs. would be the highest attainable strength in actual practice. It was soon found, however, that this was not an unduly onerous stipulation for the cement trade, and indeed it shortly afterwards became possible to raise the tensile strength considerably. Thus the clause already given was amended, so that the tensile strength demanded was 500 lbs., and the contractor was compelled to keep in store upon the works " a supply of cement equal to at least fourteen days' requirements," and with each delivery of cement he was to " send to the clerk of the works a memorandum of the number of bushels sent in, and the name of the manufacturer."

**Modification in Specification about 1865.**—Ultimately, about 1865, the clause was again amended, when it read as follows :—" The whole of the cement shall be Portland cement of the very best quality, ground extremely fine, weighing not less than 112 lbs. to the striked bushel, and capable of maintaining a breaking weight of 250 lbs. per square inch (562·5 lbs. on $2\frac{1}{4}$ square inches), seven days after being made in a brass mould, and immersed in water during the interval of seven days. The contractor shall at all times keep in store upon the works a supply of cement equal to at least fourteen days' requirements ; and with each delivery of cement shall send to the clerk of works a memorandum of the number of bushels sent in, and the name of the manufacturer."

**Tensile Strength again Raised before 1870.**—Before 1870 the standard strength was again raised, and in the specifications for the Southwark Park and subsequent works it was stipulated that the cement should be " capable of maintaining a breaking weight of 350 lbs. per square inch " (787 lbs. on the breaking area of $2\frac{1}{4}$ square inches), tested as before. Thus in a little over ten years the standard strength had been nearly doubled, and from the tables given by Mr. Grant it would appear that many samples were considerably in excess of the specified requirements ; the Burham Company having supplied over 320,000 bushels, showing an average breaking weight of 825·73 lbs. on the 2·25 square inches ; even these figures having been exceeded by certain other makers who furnished smaller quantities of the material.

**Cost of Cement Testing as Carried out under Mr. Grant.**—It is interesting to notice these facts as bearing upon the steady improvements made in the quality of Portland cement. Mr. Grant states that the entire cost incurred in testing the cement furnished during a series of years to the Metropolitan Board, during which period works to the value of upwards of £1,250,000 were executed, was about five farthings per ton of cement.

**Defects in the Early Mode of Testing.**—It is somewhat unfortunate that the tests first adopted in this country, and which have thus furnished the precedent for the majority of engineering specifications, from the fact of their being carried out with neat cement, fail to accentuate some of the most important properties of this material, among others the power of binding together various proportions of sand and other aggregates. The tensile strength, moreover, furnishes us with a knowledge of the behaviour of the cement under conditions which seldom or never come into play in actual work, and the stipulations respecting weight and fineness of grinding are somewhat loosely worded, in that they fail to indicate with sufficient precision the manner in which the weight is to be taken and the exact degree of fineness to be attained in the milling, which latter can only be shown by careful sieve-tests.

17

**Weight Tests liable to Considerable Errors.**—The mode of filling the bushel measure, which is one unnecessarily large for testing purposes, is a matter of great importance. This subject was brought under the attention of the Institution of Civil Engineers during the discussion on Mr. Grant's paper in 1865, by Sir F. J. Bramwell. He stated that " he knew by experience that when dealing with granulated matter, it was almost impossible, even with the greatest care, to get uniformity of conditions in the respective trials ; that was to say, to get the same amount of granulated material into a particular measure. In corroboration of this he would state the results of what he had tried lately. A quantity of cement was poured into a bushel measure by a man accustomed to the work, and struck off level ; it then weighed 107 lbs., exclusive of the weight of the measure. Then another portion of the same cement was poured slowly out of the sack down an inclined board into the bushel measure and it then weighed only 97 lbs. ; he then had it shaken down in the measure and the weight then got up to 132 lbs."

**Sir F. Bramwell proposed a Specific Gravity Test.**—Sir F. Bramwell pointed out that " when it was found that with the same measure of capacity and the same material there could be a variation of from 97 lbs. to 132 lbs., he could not help thinking, if a test of gravity could be obtained which was not liable to these variations it would be a very desirable thing." He further stated that the weight test " should be combined with that of sifting," an axiom that subsequent enquirers have amply confirmed. He said that if this was not done, " the requirement as to the weight was liable to act as a premium for coarse grinding." In confirmation of this assertion he adduced the following figures :—" He had sifted through a sieve of 900 holes to the square inch, a certain portion of the cement which weighed, as before stated, when very carefully put into the measure, 97 lbs., and when put in in the ordinary way 107 lbs. to the bushel ; those portions which would not go through the sieve were then poured into the bushel measure with the same care as that which made the unsifted weight, as previously stated, only 97 lbs., with this care the coarse weighed as much as 101 lbs., and when shaken down hard into the measure 144 lbs., whereas the unsifted cement had weighed, as before stated, only 132 lbs. He then took by themselves the fine particles which had passed through the sieve and they then weighed only 98 lbs. (93 ?), as against 97 lbs., and when shaken down 130 lbs., as against 132 lbs. for the mixed, and 144 lbs. for the coarse."

From these experiments he was led to believe that with the weight test, in its present form, " there might and probably would be badly ground cement present in the mass."

**Specific Gravity ascertained by Sir F. Abel.**—From some further tests on this same cement made by Sir F. Abel at Woolwich, it was ascertained that the specific gravity was 3·11, equal to a weight of 249 lbs. per bushel,

which would seem to show that if the cement could be obtained in a really solid form it would weigh 249 lbs. per bushel, the observed difference being solely due to the voids.

**Form of Early Test-Briquettes.**—All of the earlier tests under Mr. Grant were conducted, as we have seen, with briquettes having a sectional area at the point of fracture of $2\frac{1}{4}$ square inches. Mr. Reid, in his work on cements,[*] takes the credit for having suggested the pattern first used ; this was avowedly copied from French specifications, which involved the use of a briquette of the shape shown in Fig. 83, the notch forming the neck to receive the clips being cut out by hand from a solid casting after the lapse of a prescribed period of time. This must have been a somewhat clumsy plan, necessitating considerable waste of time and money, and it was, moreover, very liable, we should think, to lead to erroneous results in the tests, due to injury to the briquette during the cutting process. The French tests, on a sectional area of $2\frac{1}{4}$ square inches, were of course based upon English measurements for the benefit of manufacturers in this country, who at that period were alone able to supply the cement.
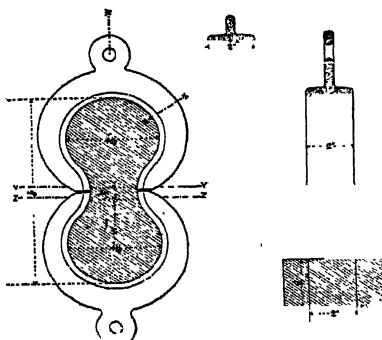


Figs. 84.
Briquette with Sectional Area at Breaking
Point of 4 square inches.
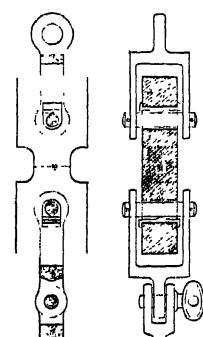
Fig. 85.
Modified Arrangement
for Testing Briquettes.

**Proposal to Increase the Sectional Area of Test-Briquette.**—At the time of reading his first paper on the subject in 1865, Mr. Grant was of the opinion that it would be advisable to modify the shape of the test-briquette and · to increase the area at the point of fracture to 2 inches × 2 inches = 4 square inches, the new form of briquette proposed for this purpose being shown in Fig. 84, with shackles made to fit the same. This new shape was, however, speedily abandoned in favour of that shown in Fig. 85. It will be seen that the clip in this case passes through an aperture in the solid ends of the

* *The Science and Art of the Manufacture of Portland Cement,* . . . by Henry Reid, C.E. London, 1877. 8vo.

briquette, small castings being inserted in each aperture so as to provide a knife-edge bearing for the shackles to strain against. These frequent changes of form, and the many efforts made to obtain reliable results in the early history of cement testing, are extremely interesting.

**Influence of the Form of Briquette on the Tensile Strength.**—In his second paper on the strength of cement, dated April, 1871, Mr. Grant gives a valuable table which we here reproduce, showing the results obtained by the use of the various forms of briquettes employed in 1866. It will be seen that ten different patterns were tried, the best results being obtained with Nos. 2 and 3, and it was, therefore, decided to employ briquettes of the former of these shapes for all future experiments. Many of these patterns were tried in order to discover the best mode of avoiding any distortion or departure from the line of strain. The plan originally adopted with this object was that shown in Fig. 84, subsequently altered as seen in Fig. 86.



It was found, however, that this modified arrangement frequently broke at the holes at each end, instead of at the neck, and it was in the attempt to avoid accidents of this kind that knife edges were inserted in the eye and pin at each end. The fiddle-shaped mould, No. 10 in table, did not break uniformly at the neck, the slightest distortion causing it to break obliquely in a diagonal line. Distortions and irregular strains were often caused by the slipping of the clips, or by the tendency of certain of the clips to open when the strain was applied, and in order to obviate this the clips were strengthened. The form first used with the sharp angles, shown in Fig. 83, often broke very irregularly, owing to imperfections in the bearing surface of the clips, and this evil was reduced to a minimum by rounding off the edges, as seen in the improved pattern, Fig. 86.

Fig. 86.
Improved Pattern of Briquette.
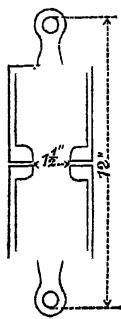
**New Shape of Briquette not a Success.**—As will be evident from the table, none of the improved shapes tested about this time gave results that were fairly comparative with those obtained with the original pattern, and this form was ultimately adopted for all subsequent tests, comprehended in the series covered by Mr. Grant's earlier papers, but in reverting to the use of the original clips, knife edges were inserted in the eye and pin at each end.

**Area of Briquette at Point of Fracture.**—Following the precedent of the German experimenters, the size of the test-briquette in common use in this country has in recent years been reduced, and it is now customary to employ briquettes having a sectional area of only 1 square inch at the point of fracture. Mr. Grant in his paper on Portland cement, read before the Inst. of Civil Engineers in May, 1880, gave some excellent instructions for

the testing of cement, which we herewith reproduce, because his long experience entitled him to speak authoritatively on this matter. He had by this time been converted to the value of the sand test and the use of small briquettes. The form employed by him in his later experiments is shown in Fig. 87.

**Instructions for Preparation of Test-Briquettes.**—The following were Mr. Grant's instructions for making the tests :—Take enough cement to make as many briquettes of either neat cement or of cement with sand, as may be required. For neat, about 3·20 lbs. of cement will be required to make ten briquettes of the smallest size of 1 inch sectional area, and 16 lbs. for ten of the larger size of 2·25 square inches area. About 1 lb. of cement and 3 lbs. of sand will make ten of the 1-inch briquettes. 500 grammes of cement, 1,500 grammes of sand, and 200 grammes of water will make ten of the German normal briquettes and allow for waste. For testing the cement in different sacks, casks, or bins, a sample may be taken from each and numbered. For experiments, or to get averages, the samples may be taken in equal quantities from each and mixed. The cement, unless it is going to be used at once, ought to be spread in a thin layer on a slate or piece of wood, and exposed to cool dry air as long as may be necessary. With newly-ground and quick-setting cements it is important to ·ascertain that they are fit for immediate use. Two cakes of neat cement 2 or 3 inches in diameter, about $\frac{1}{2}$ inch thick with thin edges, should be made, and the time noted in minutes that they take to set sufficiently to resist an impression of the finger-nail. One of these cakes, when hard enough, to be put into water and examined from day to day to



Fig. 87.—Briquette having Sectional Area of 1 square inch.

see if it shows any tendency to "fly," by cracks of the slightest kind, beginning at, and being widest at, the edges. With slow-setting cement, however, cracks on the surface, beginning at the centre, are merely the result of the surface drying too rapidly from exposure to a draught or to external heat. The other cake to be kept in air and its colour observed. A small quantity, which may be 1, 5, or 10 lbs., or 10,000 grains = 1¾ lbs., to be sifted through the three sieves of 2,580, 5,806, and 32,257 meshes to the square inch, and the proportion by weight that

will not pass through each sieve tested. The cement should be weighed, using a filler of either an imperial bushel measure, or a box of $\frac{1}{10}$ of a bushel capacity, which may be a cube of 6 inches by 6 inches by 6·16, or a cylinder of 6½ inches diameter and 6·684 inches in depth (see Figs. 88 and 89). The weight to be taken in lbs. and decimal parts. Ten briquettes to be made with three times the weight of the cement, of sand which has been washed, dried, and passed through a sieve of 20 and caught on a sieve of 30 to the lineal inch. Twenty more briquettes may be made of neat cement, to be tested as to strength after seven and twenty-eight days. The proportion of water (as of sand) to be to the cement by weight—viz., neat cement from 20 to 25 per cent. (or more) according to the fineness, the age or other conditions of the
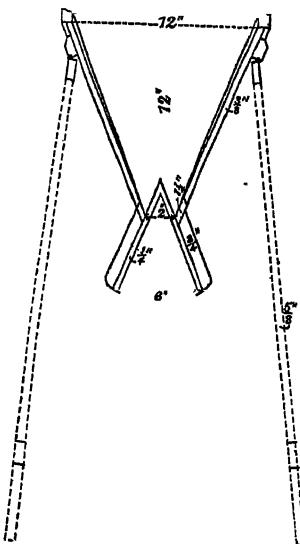


**BUSHEL.**          **LITRE.**
Fig. 88.—Filler for Bushel Measure.    Fig. 89.—Filler for Litre Measure.
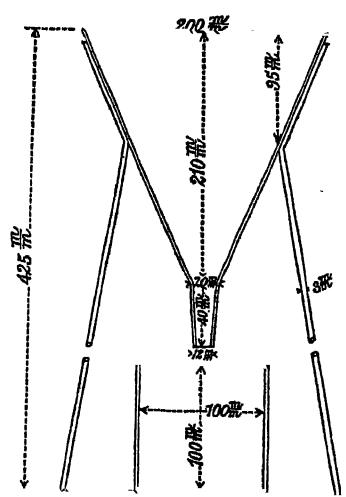
cement, and the temperature of the air. With 3 parts of sand to 1 part of cement, 10 per cent. of the weight of the united cement and sand will, as a rule, serve. Sufficient water must be used to make a stiff paste, but no more. When cement is new or hot, lightly burnt, finely ground, or made up in hot weather, it takes more water, but a very little more than is sufficient to make it into a stiff paste will sensibly diminish the strength. With 3 parts of sand to 1 part of cement the quantity of water required hardly varies from 10 per cent. A number of pieces of wet blotting-paper, a little larger than the mould, one for each mould, may be laid on the slate or marble bench, and the moulds put upon them. The moulds are filled with a small

trowel, and the briquettes made with the spatula, see Fig. 91, the mortar being beaten till all the air has been driven out and the mortar has become elastic. The surplus is cut off level, and the surface left smooth. Dr. Michaelis, of Berlin, recommends another system of making briquettes of neat cement, which, however, is not adapted for very quick-setting cements, nor for briquettes made with a mixture of sand. It is known as the gypsum-plate process. The cement is mixed with from 30 to 35 per cent. of water, and poured into moulds resting on sheets of wet blotting-paper laid upon plates of plaster of Paris. The moulds are tapped or shaken. About 50 per cent. of the water is quickly absorbed, and, if necessary, more of the cement is added. The surface having been smoothed with a trowel or knife, the briquettes are dexterously dropped out of the mould. This process is a very quick one, and Dr. Michaelis claims for it that it leaves only the amount of water which is required by the cement for setting properly, and that greater uniformity is attained than by any other process. The briquettes can thus be made denser, taking more cement, and breaking frequently under a strain about 50 per cent. higher, or even more. The absorbent slab, he compares to the brick or stone with which mortar is in practice used. But to make strong work with cement, it is necessary to soak with water bricks or stone before using them. No doubt, by long practice any one may produce uniform results by following this or any other process; but we have not succeeded in getting greater uniformity by this than we have by the process first described. When the moulds have been filled the briquettes are numbered, laid aside, and covered with a damp cloth till they have set sufficiently to be taken out of the moulds. The briquettes are then put on sheets of glass, or on slates, and laid in a flat box, having a cover lined with several layers of linen, woollen, or cotton cloth, kept damp. In this box they are kept until they have hardened sufficiently to be put into water. This will vary from one to two hours to a day or more; but for uniformity, unless in cases of specially slow-setting cement, briquettes of neat cement may be kept for twenty-four hours, and those with sand for forty-eight hours, before being transferred from this box to the shallow tanks in which they are to remain till the moment of testing. The numbers on the neat cement briquettes may be made with a sharp point or with a strong pencil. For the sand and cement briquettes, numbers previously written or stamped on small pieces of zinc will be found more convenient. The water and the testing room should be kept at a temperature as nearly uniform as possible, say, from 60° to 70° Fahrenheit; but if the box and tanks in which the briquettes are kept be covered, moderate changes of temperature will not materially affect the results.

It may be useful, especially at certain seasons, or in countries in which the temperature varies very much, to note the readings of the maximum and minimum thermometers. Seven, twenty-eight, or more days after the

briquettes have been made, their tensile strength can be ascertained. In doing this as much uniformity as possible is to be observed in applying the weight slowly and gradually, avoiding all sudden jerks. The result for each briquette being recorded, the average is ascertained.

The test with neat cement at the end of seven days is of little more use than to show approximately, by comparison with the tests made at a later date, whether the cement has increased in strength. The later tests are of most value, and especially those made with sand.

**Appliances for Testing.**—The apparatus and appliances which it is necessary or desirable to have for making tests and experiments are : a number of boxes about 4 inches deep, lined with lead or zinc, having loose covers and a tap for drawing off the water ; a similar box, which need not be lined, but the lid of which should be covered inside with several layers of coarse linen, woollen, or cotton cloth, to be kept always damp, and made to fit closely over the box ; a number of pieces of plate-glass or slates about
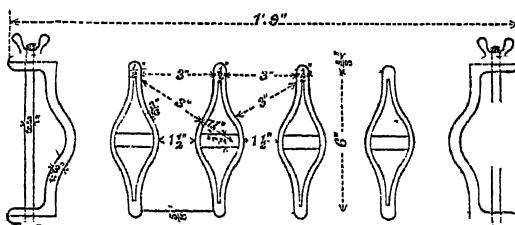


Fig. 90.—Frame for Moulding Five 1-inch Briquettes.
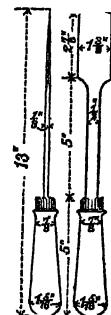
Fig. 91.—Spatula for Cement Testing.

12 inches by 6 inches, or 15 inches by 8 inches ; an imperial bushel measure ; a measure of one-tenth of a bushel, either 6 inches square by 6·16 inches deep ; or, if cylindrical, 6·5 inches in diameter by 6·684 inches deep ; scales for weighing a bushel or smaller quantities of cement, sand, or water ; weights of various denominations, including a pound and decimal parts of a pound ; 10,000 grains and decimal parts ; funnels or fillers for the bushel and smaller measures (see Figs. 88 and 89) ; brass wire sieves of 400, 900, 2,580, 5,806, and 32,257 per square inch (the first two are used for sand, the last three for cement, and correspond with the sieves used in Germany of 400, 900, and 5,000 per square centimetre) ; ten or more gun-metal moulds for making briquettes of 1 square inch sectional area (Fig. 87), and, if required, similar moulds for briquettes 1½ inches by 1½ inches = 2·25 square inches ; machine for ascertaining tensile strain (see Fig. 97, p. 277) ; a spatula (Fig. 91), with thin edges to the blade, weighing 7¼ ozs., to be used for beating the

cement and sand in the moulds ; straight-edges for striking off the measures ; a straight-bladed knife for cutting off surplus cement in making briquettes ; one or two small trowels ; two strong basins or mortars ; maximum and minimum thermometers ; blotting-paper ; a graduated glass for water ; sand, washed, dried, and sifted through a 20, and caught on a 30 meshes to the inch sieve = 400 and 900 per square inch, and forms for tabulating and registering results.

**Professor Unwin on Cement Testing.**—Professor Unwin, in the course of a paper contributed to the *Journal of the Society of Chemical Industry* in April, 1886, on this subject, points out that " testing began with comparatively crude tests of the tenacity of briquettes or test-pieces of neat cement, which at first were made of an excessively bad form, and were seldom tested after more than seven days' hardening." He proceeds to show that the defects of this plan soon became evident, and caused great differences in the apparent strength of the same quality of cement, in accordance with the amount of water used in gauging, the pressure employed in moulding, and so on.

**Qualities Needful in a Cement.**—He goes on to say that " the constructional value of a building cement depends on two quite distinct elements —on its power of setting into a rigid form soon after it is gauged, and on its power of attaining in course of time a considerable strength." We may take it for granted that no manufacturer of Portland cement at the present time would think of sending out a material incapable of satisfying the former of these requirements, though we must admit that hot over-limed cements are still occasionally met with which will set well enough for a day or two, but eventually go abroad even in the short space of the seven days' test. Such cases are, however, rare.

**The Induration of Cement takes place according to a Uniform Law.**—When ample time can be devoted to the study of the quality of any given sample of cement, and when we can note its behaviour through a long series of months or years, we shall find, as Prof. Unwin has remarked, that " beyond the first week, and up to the period at which the full strength of the cement is reached, the rate of hardening follows approximately a very simple law." The factors may be arranged in the form of a readily intelligible formula, the constants of which clearly indicate the character of the cement.

" Let $x$ be the number of weeks during which a test piece has been hardening. Then the strength $y$ in lbs. per square inch at that age is given very approximately by the equation—

$$y = a + b\,(x - 1)^n,$$

where $a$ is the strength at seven days, and $b$ and $n$ are constants depending on the rate of gain of strength with age.

" For all tension tests of Portland, $n$ may be taken as the cube root.

For ordinary limes it has a larger value. For compression tests of comparatively large blocks of Portland, $n$ is the square root; consequently, two tests of a cement at different ages determine the remaining constants of the formula."

The Professor states that the curve given by this formula reconciles the anomalies which must always occur in tensile tests, and produces an average of the somewhat discordant results. He finds by its application that neat cement tests attain their full strength in three or at most four months, while sand tests increase regularly in strength for two or three years. On working out the results from a long series of tests by Mr. Grant, he obtained for neat cement and cement mortar ($1c + 3s$) the following results :—

TESTS OF BRIQUETTES OF NEAT CEMENT AND 1 CEMENT TO 3 SAND AT
DIFFERENT AGES OF HARDENING IN POUNDS PER SQUARE INCH.

| AGE IN WEEKS. | NEAT CEMENT. | | 1 CEMENT TO 3 SAND. | |
|---|---|---|---|---|
| | Observed. | Calculated. | Observed. | Calculated. |
| 1 | 363 | 363 | 157 | 157 |
| 4 | 415 | 431 | 202 | 214 |
| 13 | 470 | 471 | 244 | 249 |
| 26 | 525 | 500 | 285 | 274 |
| 39 | 512 | 521 | 307 | 292 |
| 52 | 517 | 543 | 320 | 305 |
| 104 | 590 | 589 | 351 | 345 |
| 156 | 585 | ... | 350 | 372 |

**Specific Use of Prof. Unwin's Formula.**—In the foregoing table the value of $a$ in the case of the neat cement is, of course, 363, and in the case of the sand mixture 157 : the complete formula being—

$$\left. \begin{array}{c} \text{Neat} \\ \text{Cement,} \end{array} \right\} \ y = 363 + 48 \sqrt[3]{x} - 1.$$

$$\left. \begin{array}{c} 3 - 1 \\ \text{Mortar,} \end{array} \right\} \ y = 157 + 40 \sqrt[3]{x} - 1.$$

In the graphic diagram for these two substances on page 268 the actual tests are indicated by dots, the calculated curve is shown by the bold line.

By the application of this same method in the case of coarse and fine grinding, and for various qualities of sand, Prof. Unwin shows how the formula is affected by each different set of conditions. There is no doubt that for careful and comparative tests of cement the application of the graphic method is of great importance, and we commend to all who are interested in cement tests this very valuable and thoughtful essay.

**No Definite Limit can be Assigned for the Period of Induration.**—It is impossible to assign a fixed limit to the duration of the period within which neat Portland cement may continue to increase in strength. Some cements appear to show a slight increase in this respect up to five or six years, but these cases are exceptional, and in most dense well-made cements the in-duration has reached its maximum in under two years. After this period the briquettes in certain cases fall back slightly in tensile strength, as if some physical change took place in the structure or arrangement of the particles. Such decrease rarely exceeds 10 to 15 per cent. of the maximum strength.

**Value of Long-extended Tests.**—It is interesting and valuable to possess records of such protracted tests, and to know the exact composition of the cements with which they were carried out, as it is only by the tabulation
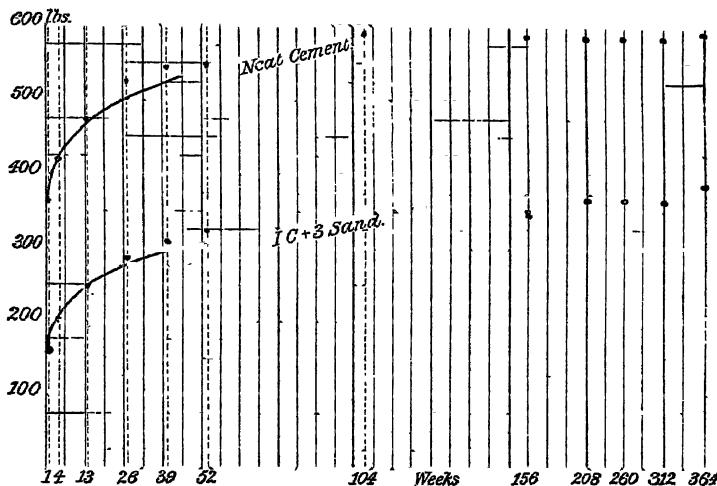


Fig. 92.—Tensile Strength of Cement and Cement and Sand Mortar.

of numerous experiments and the comparison of a large number of analyses that we can hope to acquire any accurate knowledge of the somewhat obscure changes which are slowly effected in the course of induration.

**Series of Tests of Warwickshire Cement.**—We might multiply examples to show the process of " going back " from previous works on cement, but we prefer to adduce a few original and reliable tests to illustrate our meaning. The following experiments exemplify this process in a very remarkable way. They were carried out by one of the authors with some Warwickshire cement in 1888.

The sample in question was burnt extremely hard, and was of a dark blue colour. It was ground so that it all passed a 50 × 50 mesh sieve.

## CHEMICAL ANALYSIS.

| | | |
|---|---|---:|
| Insoluble residue, | . . . . . . . | 4·557 |
| Silica, . . | . . . . . . | 16·865 |
| Ferric oxide, | . . . . . . . | 4·831 |
| Alumina, . . | . . . . . . | 6·360 |
| Manganese oxide, | . . . . . . | trace. |
| Lime, . . | . . . . . . | 62·507 |
| Magnesia, . . | . . . . . . | 2·365 |
| Sulphuric acid, . | . . . . . . | 1·589 |
| Potash, . . | . . . . . . | ·976 |
| Soda, . . | . . . . . . | ·527 |
| | Total, . . . . | 100·577 |

## TESTS OF THE ABOVE CEMENT.

Neat cement, water 16 per cent.   The mixture set slowly.

| 7 days. | 28 days. | 90 days. | 550 days. |
|---|---|---|---|
| Lbs. | Lbs. | Lbs. | Lbs. |
| 515 | 630 | 710 | 695 |
| 500 | 630 | 760 | 670 |
| 600 | 620 | 730 | 685 |
| 660 | 650 | 800 | 660 |
| 650 | 650 | 780 | 655 |
| 630 | 660 | 750 | 685 |
| 620 | 570 | 760 | 660 |
| 650 | 600 | 790 | 655 |
| 615 | 620 | 750 | 705 |
| 690 | 620 | 815 | 675 |
| | Average | of 10 tests. | |
| 613 | 625 | 764·5 | 674·5 |

Cement 1 part, standard (Leighton Buzzard) sand 3 parts by weight, water 10 per cent.

| 7 days. | 28 days. | 90 days. | 550 days. |
|---|---|---|---|
| Lbs. | Lbs. | Lbs. | Lbs. |
| 185 | 205 | 220 | 310 |
| 200 | 210 | 215 | 290 |
| 200 | 220 | 200 | 305 |
| 200 | 215 | 205 | 335 |
| 195 | 200 | 215 | 300 |
| 210 | 215 | 205 | 295 |
| 200 | 225 | 230 | 300 |
| 210 | 205 | 200 | 240 |
| 195 | 225 | 215 | 325 |
| 200 | 205 | 240 | 325 |
| | Averages. | | |
| 199·5 | 212·5 | 214·5 | 302·5 |

**Critical Period during Induration.**—In the above tests it will be observed that the values for the neat cement indicate a decided falling off between the 90 days' test and that at 550 days, and all observers who have carried out corresponding experiments will have noticed the intervention of such a critical period, generally before the end of the second year, especially in very dense cements. No such decrease in strength is apparent in the sand tests, and it is probable that some molecular changes occur during the induration which are not yet understood. This critical period does not always occur after the same interval, and it varies in accordance with the composition of the cement, the temperature at which it has been fired, and the degree of density that it has attained. A well-known writer on Portland cement has attempted to explain away this falling off in strength and to attribute it solely to carelessness in testing. He even says concerning some breaking weights which indicate just such a diminished strength—" It is to be hoped that no more of these records of questionable value will be published, for their misleading and uncertain character has already created too much scepticism on the possibility of cement improving in value."

**Present Methods of Testing Cement.**—Specifications now not only state the requirements, but usually also the conditions to be observed in making the tests. With certain additions and modifications, the system adopted by Grant for mechanical testing, which has been described earlier in this chapter, is a good one even for present-time use, but in consequence of the greatly improved quality of cement as compared with that in his day, much higher results are now required from the tests. The weight per bushel, or volume weight, has been discarded in favour of the specific gravity, which we have dealt with in Chapter VIII. The chemical composition is frequently controlled, especially as regards the content of magnesia and sulphuric acid. Constancy of volume or soundness is generally determined by some form of accelerated or heat test. These tests will be described in the following chapter, but it should be noted that Grant's method of preparing a cake of cement about ½ inch thick, made on a glass plate and thinned down at the edges, which is immersed in water after setting and kept under observation, is in Germany still regarded as the conclusive test for soundness.

**Sampling.**—When sampling from bulk, care should be taken to avoid the surface that has been exposed to the air. The heap, or silo, should be well broken into at several places from which samples are taken, and mixed together to obtain an average. An effective apparatus for sampling from bulk has been devised by Bertram Blount. By short lengths of pipe, screwing one into the other, any part of a heap or silo may be reached. After insertion, the pipe is connected by a flexible tube with an air-tight cylinder, to which suction is applied by a vacuum pump. This causes a stream of cement to flow into the cylinder, and samples from as many places as may be desired are taken. The top of the cylinder is provided with an opening, closed by

an air-tight cover, for removing the contents. Casks may be sampled by boring holes in them and withdrawing samples by means of a long twisted rod sharpened like a drill. The twisted portion should be of sufficient length to reach, when in use, to the outside of the cask. It is difficult to take accurate samples from bags, as the contents, especially when in contact with the bag, will have been affected by the moisture of the air, while the centre portion may have been unacted upon. A fair sample may be obtained by emptying and well mixing on a clean floor the contents of a few bags, from which a sample is taken.

**Determination of Fineness.**—This is usually made by sifting a specified weight of cement, usually 50 grammes, for a given length of time, the sieves used being of woven brass wire of 180 or 200 meshes to the lineal inch, and weighing the residue.

Several instruments have been devised for effecting the separation of the finest flour by means of a current of air ; three of them may be noticed.

**The Goreham Flourometer.**—This is a simple piece of apparatus for separating from a sample of cement all the very finest particles (flour), and for estimating the relative proportions between fine and coarsely-ground material. In using the flourometer, a fixed quantity of the cement to be tested is placed in a special receptacle, and air is forcibly driven through it, which causes the cement flour to separate from the residue. All those particles which are sufficiently light are carried through the upcast tube, and then sink to the bottom of the settling chamber. When all the flour has thus been expelled, the residue, which consists of the coarser particles, is weighed, and the difference between the weight of the residue and the weight of the entire sample indicates the amount of the flour, which latter can readily be expressed as a percentage of the whole amount. A good sample of cement should yield from 40 to 50 per cent. of flour by this test. The War Office authorities specify a minimum of 45 per cent. It is asserted that this test is much more reliable than the sieve-test, and that no cement which yields less than 42 per cent. of flour will show good results in practical work.

The apparatus consists of an aërometer for providing the necessary supply of air at any desired pressure, and the flourometer itself, with which the separation is effected. The weight of cement to be used for each test (preferably 40 grammes) is placed in a glass vessel provided for the purpose, and the rubber tube connected with the aërometer is then attached. Each test requires about 45 minutes, and the inventor recommends that the resulting flour should be examined under the microscope, and also tested by rubbing it on a piece of glass with a palette knife, to see that it is not gritty. Unless care is exercised in carrying out the test, it is possible that all the flour may not be entirely removed from the sample, or that a little of the residue may be carried over into the settling chamber. This apparatus

is, however, undoubtedly capable of furnishing useful and reliable information respecting the quality of cements.

**The Gary-Lindner Apparatus.**—This is represented by Fig. 93. The tubes I, II, III are connected by rubber sleeves with small cones closed at the ends, into which glass tubes reaching nearly to the bottom are fused. They are connected to branches in the air tube below by rubber tubing. The branches are provided with stop cocks. Twenty grammes of cement are introduced into cone I, and dry air at a pressure of 100 millimetres of water admitted, which passes successively through I, II, and III. The operation is complete in 20 minutes, the finest flour is collected in the glass vessel at the bottom of Tube IV, the residues remain in the cones of the other tubes. The following results have been obtained with this instrument :—The fine flour from an ordinary cement that contained 17·4 per cent. of residue when tested on the sieve of 180 meshes to the lineal inch was 26·6 per cent. In the same cement, after sifting through the 180-sieve, the siftings gave 31·2 per cent. of fine flour.

**The Mayntz Petersen Apparatus.** — This is much simpler than the Gary-Lindner. It consists of a glass cylinder with restricted top and long conical base, connected to an air blast of fixed volume and speed. Ten grammes of cement are introduced and the air admitted, the flour escapes through the top, and the residue is withdrawn at
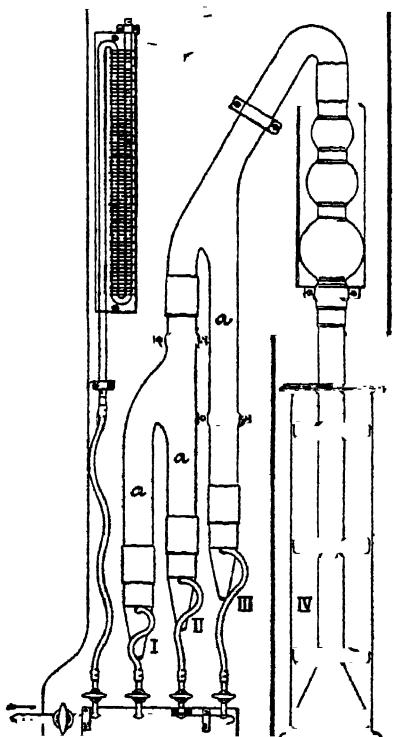


Fig. 93.—Gary-Lindner Apparatus for determining the Fine Flour in Cement.

the base. In an experiment, ten estimations of the same sample gave a difference of only ·2 gramme.

**Time Required for Setting—The Vicat Needle.**—In the previous chapter, we have mentioned that the setting time of cement may be regulated, and a definite time is often specified. The British Standard Specification defines three rates of setting—quick, medium, and slow. The Vicat needle, which

is illustrated by Fig. 94, is the instrument in most general use for determining the time of setting. It consists of a frame in which a rod surmounted by a cap slides easily. To the rod a pointer is attached, which indicates milli- metres on one side of a graduated scale and inches divided into twentieths on the other. The rod with cap weighs 300 grammes. The needle, 1 square millimetre in section, is fixed in a small brass cylinder, which fits in a socket at the end of the rod in which it is secured by a screw. A cylinder, 1 centi-
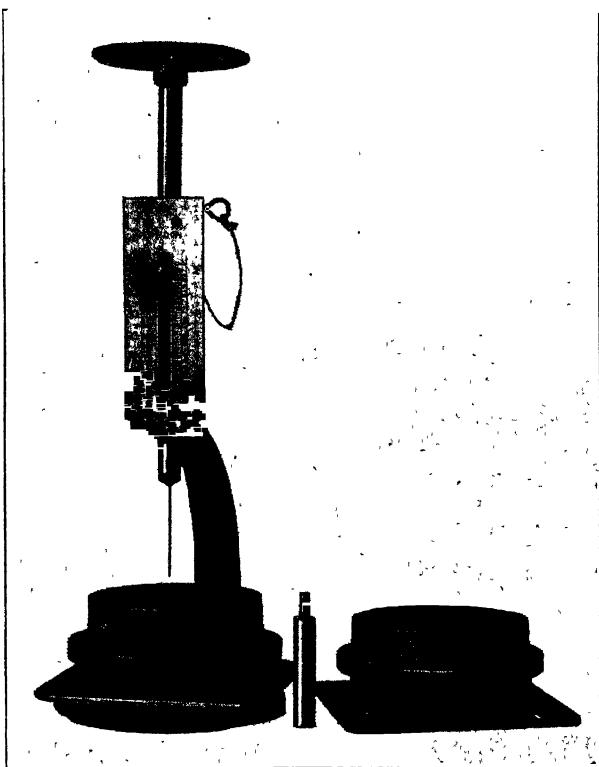


Fig. 94.—Vicat Needle for determining the Setting Time of Cement.

metre in diameter, also fits this socket. The moulds are of brass, in halves clamped together by a brass ring, and rest on iron plates.

To make an experiment, a mould is filled and levelled off smoothly with cement gauged to the proper consistency. To determine this, the cylinder of 1 centimetre in diameter in which the rod is secured is carefully held on the surface of the cement in the mould, which is placed beneath it, and is then

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allowed to sink by its own weight, and, of course, with that of the rod and cap. The consistency is correct when it rests at a height of 6 millimetres from the bottom of the mould. The quantity of water required for gauging is a matter of experiment, and is arrived at by repeated trials with weighed quantities of cement and measured quantities of water. The correct consistency being arrived at, the cylinder is removed and replaced by the needle, which on being gently liberated at the surface of the cement will sink to the bottom. This operation is from time to time repeated, and when the needle ceases to reach the bottom setting is considered to have commenced, and to be complete when it ceases to make an impression on the surface of the cement. If a scum forms on the surface, the under side of the block should be used for determining the complete or final set.

A definite consistency is frequently not regarded. The mould is filled with cement gauged to a stiff workable condition, and the penetration of the needle is read off on the scale at the commencement of the experiment.

As will be understood from the description, frequent attention is required from the operator during the progress of this test, and with slow-setting cement the process is a tedious one.

**The Spissograph.**—This apparatus, the invention of Mr. R. Gordon Nicol, Engineer to the Aberdeen Harbour Board, derives its name from the Latin word *spissare*, to thicken. It tests automatically and records on a diagram the initial and final setting time of cement, and once set working requires no further attention until the operation is complete. It consists of a clockwork mechanism, which can be arranged to lower and raise the needle and weight every $2\frac{1}{2}$ minutes for a quick-setting cement and every 5 minutes for a slow-setting one. At the same time, the mould containing the cement rotates in a spiral course by the action of the clockwork, thus continually exposing a fresh surface to the needle. The apparatus is enclosed in a case provided with a glass front. A thermograph records on the diagram the temperature at which the test was made, and, if desired, a thermostat with a gas burner and regulator may be used to maintain any desired constant temperature. Fig. 95, illustrates the apparatus without the case.

**Tests for Strength.**—Although in practice cement is not used in tension, it is usually tested by its resistance to tensile strain, and this is the standard test for strength both in England and America. In Germany, the standard test is by compression, but, in certain circumstances, tensile tests are made, a definite relation being established between them. As regards this, particulars are given in our translation of the German Standard Rules in Chapter XXIV. The relation between compression and tension is usually taken as about 10 to 1. For tests by tension small machines of moderate cost are suitable, while, for those by compression, large and costly machines are necessary, and this has probably to some extent influenced the retention of tensile tests.

Grant's method of making briquettes, which we have previously described, may be still employed, but it is now the practice always to place them in water at the end of 24 hours after moulding. Instead of making the sand briquettes on a bench or slab, we prefer to make each on a separate plate with a mould held together by a spring. After filling and levelling, the mould is carefully removed and the briquette with plate placed in the
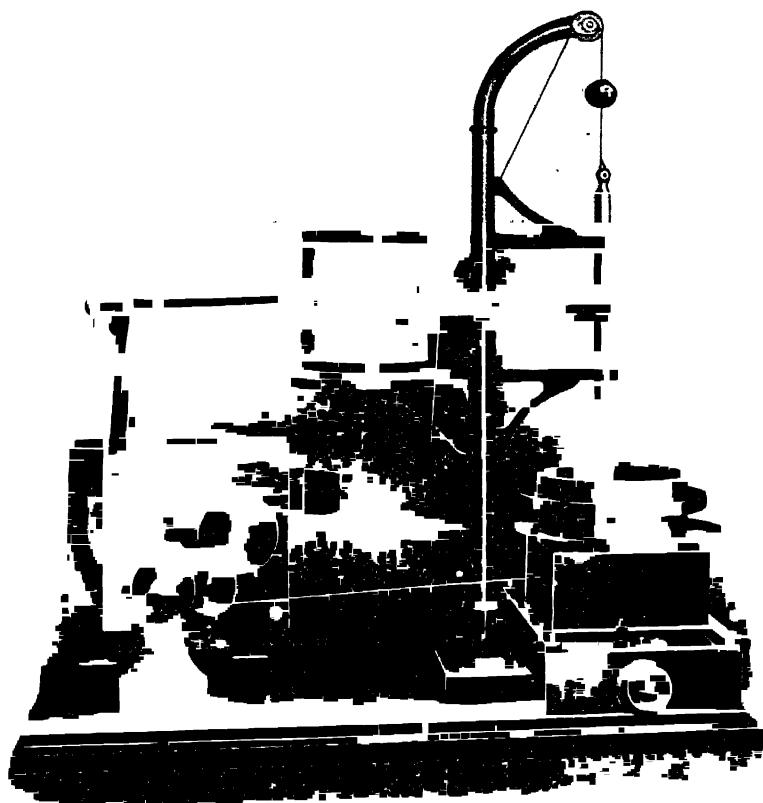


Fig. 95.—Nicol Spissograph.

damp closet or box until the time for immersion, when it is raised from the plate. The blotting-paper prevents the mould and briquette slipping on the plate. Machines for mixing are not generally used in England, in Germany their use is general. Cement alone is easily gauged with a trowel on a slab, but sand mixtures are troublesome to prepare in this way. A better plan is to

use a cream basin and a wooden spoon. Weighed quantities of cement and sand sufficient for the required number of briquettes are put into the basin, and thoroughly mixed dry with the spoon. Water for the required consistency is then added and the contents of basin are again thoroughly mixed.

Standard sand is obtained from the Leighton Buzzard pits in Bedfordshire. It is washed, dried, and after passing through a sieve of 20 must be retained on one of 30 divisions to the lineal inch.

The standard briquette is shown by Fig. 96. It differs from Grant's form only in shape of the ends, the essential—the neck—is the same in each, both being struck from a $\frac{3}{4}$-inch radius.

**The Adie Testing Machine.**—One of the oldest and best-known cement testing machines was that made by Mr. Patrick Adie, of Westminster, Broadway. It is used by many Government departments, and has long been considered the standard apparatus in this country. The maker states that his chief aim in the construction of his machines has been to secure the most accurate and undeniable results, with absolute permanence and non-interference of the hand of the operator; thus, all springs and screws are dispensed with, and the simple steel lever, and vernier (with weight attached) travelling on rollers, is adopted. The vernier is caused to travel along the lever by means of a cord, passing over pulleys fixed to the standards, and thus all need of applying the hand to the lever during

Fig. 96.—Standard Form of Briquette.

the progress of the test is avoided. In order to make this more unquestionable, in addition to the speed-reducing wheel and pinion, a patent automatic regulator can be added. As there are no compound levers, spring balances, or other appliances liable to give a multiplied error, or to be in any way uncertain in action or unreliable in results, this machine has everything in its favour, and compares well with other forms of testing apparatus. We illustrate the No. 2 machine of Adie (see Fig. 97), made with automatic regulator, but a somewhat simpler form of machine can also be supplied.

By causing the weight to travel swiftly along the lever a greater apparent strength may be obtained from the briquette under test. The strain should be applied at the rate of 100 lbs. in 12 seconds.

**The Michaelis Testing Machine.**—As shown by the illustration (Fig. 98), this is a double-lever machine, the proportion of the upper lever is 10 to 1, of the lower 5 to 1, a total leverage of 50 to 1. The strain is applied by small shot falling into the bucket suspended from the end of the upper lever. The rate of flow from the receptacle can be adjusted, and the stream of shot is automatically cut off by the falling of the bucket when the briquette breaks. The weight of the bucket and shot multiplied by 50 is the breaking strain
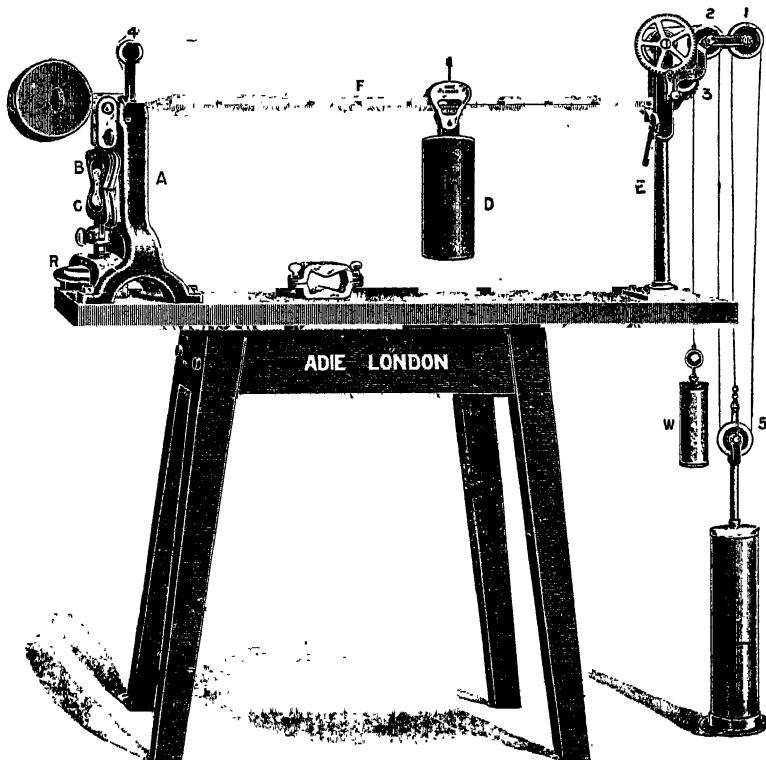


Fig. 97.—The Adie Testing Machine.

of the briquette. It is placed on the spring balance shown on the left of the illustration, the breaking strain being read off from the dial. This is the standard machine in Germany for tensile tests, and is also largely used in this country. It is made by Adie, who has adapted it to English weights and measures. The illustration shows the German form of briquette.

**Arnold's Method of Cement Testing.**—A method of testing cement, devised by Mr. Arnold, deserves passing mention, as it no doubt eliminates some

of the imperfections in our present system which arise from the differences in handling which it is impossible altogether to avoid.   We all know that
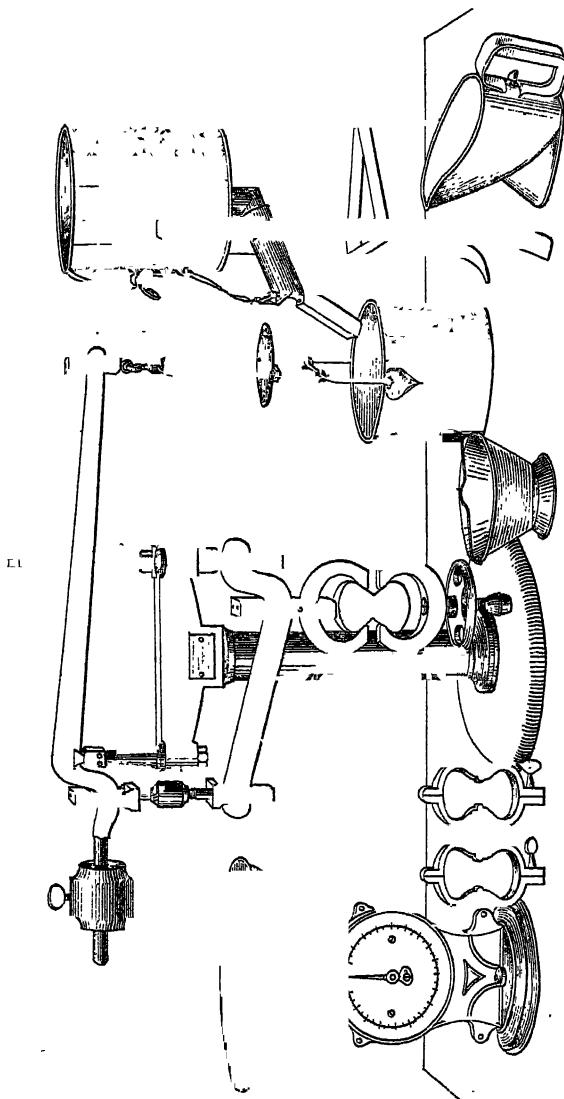


Fig. 98.—Standard Machine employed in Germany and Austria for Testing Cements.

one man will get results some 10 or even 20 per cent. better than another with the same sample of cement.   Mr. Arnold's method consists in filling

the mould for the test briquette with a proper quantity by weight of the dry neat cement, which is then consolidated under a screw-press, resembling in construction an ordinary office copying-press. The plate on which the moulds rest has shallow sides, thus making it a bath. After removal from the press, each mould having been separately pressed, the bath is filled with water (when full it contains a depth of about ¾ of an inch), and the moulds stand therein for twenty minutes before removal. The moulds are made deeper than is required for the section of the briquette. Metal dies which exactly fit the mould are placed upon the top of the cement before it is inserted in the press, so that when the die is properly pressed down, its top is level with the top of the mould and no further compression can take place. Thus a uniformity of pressure is insured in the case of each briquette moulded from the same sample of cement. In order to avoid difference arising from varieties in the bulk of different qualities of cement, it is pointed out that dies of various thicknesses can be used. It is claimed for this system of making briquettes that much greater uniformity is attained than by the plastic method, that the services of an experienced man are not required, that the requisite amount of water and no more or no less is used, and that air bubbles are entirely avoided. The patentee states, moreover, that the evidence of a blowing cement will be noticed in 24 hours after moulding the briquette, and that owing to the absence of disturbance, after admixture with water, any particles of free lime present are invariably detected at the point of fracture.

# CHAPTER XVII.

## ACCELERATED TESTS FOR CONSTANCY OF VOLUME.

CONTENTS.—Reasons for such Tests—The Origin of the Boiling Test—Tetmajer's Test
—Maclay's Test—Erdmenger's Test—Prüssing's Test—The Heat Test of Heintzel
—Faija's Test—The Le Chatelier Test—Practical Results of Accelerated Tests—
Verdict in Germany.

**Reasons for such Tests.**—A desire has constantly been expressed by cement users from the earliest period when cement became subjected to regular tests, for some more rapid means of ascertaining the reliability of the material than the ordinary tensile tests carried out with suitable briquettes at fixed intervals spread over a considerable period of time. The announcement, therefore, of the discovery of a method of forming an opinion concerning any sample of cement in a few hours was hailed with satisfaction, and the new tests were widely accepted by engineers and manufacturers, without any very searching enquiry concerning their practical utility and value.

**The Origin of the Boiling Test.**—We owe the boiling test in its original form to Dr. Wm. Michaelis, of Berlin, who, some 29 or 30 years ago, described a system of dealing with cement samples in the following way :—Fifty grammes of the material to be tested were made up with about 13 to 15 grammes of water to a paste of normal consistency, and thoroughly worked with the trowel for about one minute, to expel air-bubbles. The cement mortar was then spread in pats on glass plates, the pats were to be about 1 centimetre thick in the centre, and to be thinned out all round the edges in the usual way. The pats were allowed to set for 24 hours in a covered vessel in an atmosphere saturated with moisture or steam vapour. They were then introduced either while still on the glass plate, or after being detached from it, into a water-bath ; the water was at first quite cold, and just sufficient water was used to cover the pats completely. The water was then slowly raised to the boiling point in about ten minutes, and maintained at boiling temperature for three hours, after which the pats were taken out and examined. If any extra water was needed to maintain the level in the water-bath, it was to be added in small quantities at a time, and as nearly at the boiling temperature as possible. A sound cement would stand this test without any sign of cracking, and become considerably harder for the boiling, while it was contended that a treacherous or unsound cement would either crack all to pieces in the bath, or it would go abroad

(*i.e.*, crumble) into mud. Sundry slight modifications in the procedure have been proposed. Thus, the sample pats were directed to be made up on moistened blotting-paper, placed on a glass plate, and allowed to set, after which the blotting-paper was removed and the tests were conducted as before.

**Tetmajer's Test.**—Professor Tetmajer advocated a very similar plan of conducting the experiment, only he employed the cement made up into little balls about 2 inches in diameter, and of such a consistency that they could be patted down on a glass plate and flattened out by the pressure of the hand into circular pats, free from cracks. The pats thus prepared were to be kept in a damp atmosphere for 24 hours, and were then placed in a cold bath, which was brought up very slowly (in $1\frac{1}{4}$ hours) to the boiling point, and boiled for six hours continuously.

**Maclay's Test.**—Maclay proposed a modification of the Tetmajer test for use in America, and he employed four pats of neat cement, made up on glass plates with water into a very stiff consistency. These pats were to be about $\frac{1}{2}$ inch thick and 3 inches in diameter. One of these pats was to be placed, directly it was made up, in a steam oven at 90° to 95° Centigrade. The second pat was to be placed in the oven when it had become set hard enough to resist penetration by a normal test-needle, loaded with a weight of 1 lb. ; while a third pat was to be allowed double the setting period indicated by the previous test before being introduced into the oven. The fourth pat was only placed in the steam oven after 24 hours. The four pats remained in the steam oven at the temperature indicated for three hours, and they were then placed in boiling water for 21 hours, when the test was complete. If the cement is very defective owing to excess of free lime, improper burning, or other causes, the trouble generally shows itself in the cracking or distortion of all four pats. When the cement is not so bad, the cracking and swelling takes place in the first three pats only, and when the cement is still less defective only the first two pats crack or swell. Failure in No. 1 pat can, as a rule, be disregarded. For the United States Army Department tests the boiling is to last for six hours.

**Erdmenger's Test.**—Dr. Erdmenger was in favour of an even more severe test than simple boiling, and he has arranged a special apparatus in which the samples of cement can be boiled under a pressure up to 40 atmospheres. Dr. Michaelis has also designed a similar apparatus for subjecting samples of cement to boiling under pressure, and he recommends that the test should be conducted at 450 lbs. per square inch. Certain interesting results with respect to the induration of cements have been studied under these very severe conditions, but it can scarcely be maintained that tests of this rigid kind should be imposed upon all cements, for many materials which have been found to give excellent results in practice have failed entirely under these onerous conditions. This test has received considerable attention

in the United States, and much experimental work has been done with it.
It is there known as the " autoclave " test.

**Prüssing's Test.**—Some of the special accelerated tests involve the treat-
ment of cement by processes which would appear to be very unfair to this
material from the point of view of chemical action and the generally-accepted
theories of induration. Thus Prüssing advocates that 100 grammes of cement
should be made up into a paste with from 5 to 8 per cent. of water, in accord-
ance with the fineness of the grinding, and very intimately mixed ; indeed,
he specifies rubbing the mixture through a sieve having 120 meshes to the
square centimetre, after which it is to be spread uniformly into a mould
and stamped into a cake in a press at 50 atmospheres pressure. Two such
cakes, directly they are taken out of the moulds, are laid on a glass plate,
and are placed in a box where they are protected from evaporation. They
remain for 24 hours to become set, and are then transferred to a vessel of
cold water. One of the cakes remains under water for 28 days to indurate,
and the other is taken out in two hours' time, and, if it is uninjured, it is
placed in a water-bath at a temperature of from 90° to 100° C. If, after
remaining four hours at this temperature, the pat is still uninjured
and free from cracks, the cement may be pronounced safe under all
ordinary circumstances, but it is usual to let it remain for twenty
hours longer in the water-bath at the boiling point. It is to be regarded
as entirely reliable and especially sound and good if it stands this
treatment.

**The Heat Test of Heintzel.**—Certain of the tests appear to be somewhat
whimsical and fantastic. Among these we may mention the red-heat test,
under which a ball about 5 centimetres in diameter, formed of neat cement,
is moulded in the hand, and the quantity of water necessary, which may
be about 20 per cent. of the weight of the cement, is found to be that which
will slightly soil the hand, but will leave the ball capable of being pressed
into shape while being handled. With quick-setting cements rather more
water is needed ; thus, taking 300 grammes of cement, up to 62 or 63 cubic
centimetres of water may be employed with advantage. The ball, when
ready, is laid on a plaster of Paris slab for about five minutes, or so long
that it will no longer readily mark with the finger-nail, and it is then placed
on a thin iron plate or on a wire triangle, and is supported over the flame
of a Bunsen burner. The point of the flame must at first be kept well below
the test, for if heat is applied too rapidly, little splinters, due to the steam
evolved by the moisture in the ball, will be thrown off. As the ball dries,
the flame is brought nearer and nearer, until it entirely surrounds the ball,
and this may take place in about half an hour. During the second half-
hour the bottom of the ball attains a dull red heat, and a plate of cold glass
held above it ceases to show any condensation due to escaping moisture.
The test is then complete, and if the ball remains sound, the cement may be

pronounced to be of excellent quality. This very stringent test was devised by Heintzel, but it has never been very widely employed.

There are several varieties of these tests, some of them requiring considerable skill in conducting them, and this would, therefore, render them rather unsuitable for uniform tests.

**Faija's Test.**—Several forms of the hot-water test have been carried out in this country, but perhaps that of Mr. Faija is most widely known. It is based on the principle that moist heat accelerates the setting of cement; and it is asserted with some good show of probability that boiling means seasoning, and that a few hours in the water-bath at the boiling point are equivalent to as many days in damp air under ordinary conditions. The apparatus for conducting the test consists of a covered vessel in which water is maintained at an even temperature of from 110° to 115° F.; the space above the water is, therefore, filled with the vapour rising therefrom,
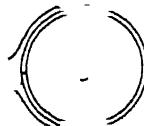


Figs. 99 and 100.—Instrument for the Le Chatelier Test for Soundness.

and is at a temperature of about 100°. Immediately the pat is gauged, it should be placed on the rack in the upper part of the vessel, and in five or six hours it may be placed in the warm water and left therein for nineteen or twenty hours. If, at the end of that period, the pat is still fast to the glass, or shows no signs of blowing, the cement may be considered perfectly sound; should, however, any signs of blowing appear, the cement should be laid out in a thin layer for a day or two, and a second pat be made and treated in the same manner, as the blowing tendency may only be due to the extreme newness of the cement.

**The Le Chatelier Test.**—This test requires a special instrument, which is shown by Figs. 99 and 100. It consists of a cylinder made of hard brass, 5 millimetres in thickness, 30 millimetres in diameter, and 30 millimetres long, which is split in the direction of its length. On each side of the split, two needles or indicators are attached which are pointed at the ends, the distance from the ends to the centre of the cylinder is 165 millimetres

(6½ inches). To make a test the cylinder is placed upon a glass plate, and filled with a sample of the cement to be tested, gauged to the proper consistency. It is covered by a glass plate and a small weight, and is then carefully immersed in cold water. At the end of 24 hours it is removed from the water, and the distance between the points measured. It is again placed in cold water, which is brought to boiling in about 30 minutes, the boiling being continued for six hours. After removal from the water, and cooling, the distance between the points is again measured. The difference between the measurements is the expansion of the sample, which is considered as a measure of the soundness. This is the accelerated test required by the British Standard Specification, which allows a maximum expansion of 10 millimetres with cement aerated for 24 hours, after 7 days' aeration 5 millimetres.

**Practical Results of Accelerated Tests.**—As the result of the methods under which these accelerated tests are conducted, it is generally assumed that their effect is to indicate constancy of volume or " soundness," but it will readily be perceived that this does not necessarily follow. Many samples of cement which are found to give excellent results in practice, when made up with sand in the usual way, are reduced to mud, and lose all traces of cohesion under the boiling test. It must be remembered that all these heat tests expose the sample of cement to highly artificial conditions, and to such as would certainly not be found in the natural use of the material. They are, in fact, many of them, so radically different from the conditions experienced by mortars or concretes in ordinary engineering practice, that it is safe to say that the results they yield can only be regarded with considerable suspicion. All the circumstances, moreover, which tend to accelerate the chemical and physical processes of induration in the natural use of the material, can hardly fail to be distorted and interfered with by the application of rapid heat, and the employment of the boiling process. In an ideal system of acceleration, the aim should be to make use of procedures which differ as little as possible from the circumstances attending the use of cement in the ordinary methods of engineering practice. It is hardly possible to conceive that the heat test, for instance, of Heintzel could prove otherwise than injurious to a slow-setting cement; and, if the induration of a cement is to any extent due to a process of crystallisation, prolonged boiling would certainly be most inimical to a satisfactory issue.

**Verdict in Germany.**—The German Union of Cement Manufacturers, when these tests were introduced, took measures, by the appointment of a Commission, to ascertain how far the practical results of employing cements in construction coincided with the verdict of the laboratory and the outcome of the accelerated tests. From an excellent report by Mr. Gary, who represented the laboratory in the work of the above Commission, we gather the following facts :—

Cements, none of which would pass the boiling test, were procured from ten different manufacturers in various parts of Germany, under conditions affording entire secrecy.  As soon as they were received they were submitted to tests in three different laboratories, and portions of each were also used in the preparation of cement wares, to be exposed to the weather.

Though the figures representing the laboratory results varied somewhat considerably under the hands of the several experimenters, the general results were easily reconcilable, and were upon the whole satisfactory, while the practical examples from the workshop, consisting of medallions, rosettes, and pipe caps moulded in cement, with the exception of a few unimportant cracks round the rims, set hard and stood well under exposure to the weather. Apart from the fine hair cracks, all the objects, after more than two years' hardening, were pronounced " still sharp cut and in good condition."

## CHAPTER XVIII.

## THE CONSTITUTION, SETTING, AND HARDENING OF
## PORTLAND CEMENT.

CONTENTS.—Early Researches—Modern Methods of Research—The Work of M. Le
Chatelier—The Work of Tornebohm—Messrs. S. B. and W. B. Newberry's Experi-
ments on the Constitution of Hydraulic Cements—Rankin's Researches—The Work
of Bates and Klein—The Crystalline Theory of Setting and Hardening—The Colloidal
Theory of Setting and Hardening—Researches of Klein.and Phillips—Dr. Rosen-
hain's Theory of Setting and Hardening.

**Early Researches.**—We have in Chapter VI. given an account of the raw
materials suitable for the manufacture of Portland cement, from which
the object of the manufacturer is to prepare a mixture which on the addition
of water will speedily attain a notable degree of hardness or induration,
and will be capable of uniting together a considerable quantity of sand or
other aggregates in the form of mortar or concrete.

In the selection of materials for the manufacture, the chief object to
be attained is that lime, silica, and alumina, the essential constituents,
are present in suitable proportions in the mixture, to enable them to be
brought into the required combinations during the calcination process.
The reactions between the various components when exposed to great heat
are complex and difficult to study, as are also those taking place during the
period of setting and hardening.

The properties of the hydraulic limes and cements have been the subject
of investigation by many observers for more than a hundred years. Jordis
and Kanter give a bibliography * of 150 publications in various journals
dealing with this subject, commencing with the work of Vicat and Berthier
in 1820, and coming down to that of Le Chatelier, Michaelis, Clifford Richard-
son, and others in 1902 and 1903. In a critical review of the work of this
period they state that much of it is valueless, being based either upon in-
sufficient evidence or upon none at all. Much of this work was no doubt
founded upon results obtained from analyses of cement, which, although
showing the constituents present, give no indication of the manner in which
they were combined.

**Modern Methods of Research.**—The methods which are now employed
for researches on the constitution of Portland cement are the microscopical

* *Zeitschrift für Angewandte Chemie*, vol. xvi., 1903.

and the synthetic. For microscopic investigation thin sections of clinker, so thin as to be transparent, are examined in transmitted light. This distinguishes transparent and opaque constituents, and by the aid of the polariscope their optical properties may be determined. Thin sections of clinker are not easy to prepare, and as the constituents usually merge one into the other, it is difficult to distinguish them or to determine their optical characters.

Another microscopic method of examination is by reflected light. A small piece of clinker is ground to a flat surface, which, after etching, can be examined by an ordinary microscope to which an illuminator is fixed in the tube above the objective. The constituents are clearly shown, but it is not possible to determine their optical characters by this means. Good photographs may be obtained by its use, and these may be compared with standard photographs obtained from thin sections of normal clinker that have been examined by transmitted light.

Much light has been thrown on the constitution of Portland cement by the synthetic method. By this, all the possible compounds of the only essential constituents of silica, alumina, and lime are prepared from absolutely pure materials, and the characteristic properties of each are studied. The non-essentials, iron, magnesia, potash, and soda, which occur as impurities in the cement raw mixture are not regarded. They act in the kiln as fluxes and lower the eutectic temperature.

**The Work of M. Le Chatelier.**—The early work of Le Chatelier on the constitution of Portland cement was communicated to the Paris Academy in 1882. On examining thin sections of clinker by the polariscope, he found that the mass was composed undoubtedly of a variety of chemical compounds. It was quite impossible to isolate each of these small particles for analysis, but he was able by synthesis to build up from lime, silica, and alumina, the different bodies which he recognised as forming part of the clinker, and he ascertained that these substances, when viewed with polarised light in the microscope, are really the compounds he found in the clinker.

These he describes as follows :—

1. A substance which has no action on polarised light. It consists of aluminate of lime rich in lime, occasionally mixed with particles of free lime. He actually produced by artificial means a tricalcium aluminate, $3CaO.Al_2O_3$, he assured himself that this crystallises in the cubic, consequently, polariscopically inactive system, and that, moreover, it is the only possible compound of lime capable of being present in cements besides lime itself, which crystallises in this system.

2. A substance acting feebly on polarised light and presenting a clearly defined crystalline form. This is a silicate of lime. M. Le Chatelier conceived this to be the chief, if not the only active, ingredient of cements ; this substance always constituting the principal part and sometimes the

entirety of Portland cements. He believed himself in a position to affirm that it is a calcareous peridot (lime olivine), $2CaOSiO_2$, which, upon the calcination of the cement, crystallises in the matrix described in the next paragraph, when the whole is carried to the point of fusion.

3. A substance having a deep brown colour, which acts upon polarised light. This is the most fusible of the components of cements. It constitutes in the solid form the gangue of the silicate which has just been described, and when melted it is the cause of its crystallisation. It is an alumino-ferrite of lime, having less lime than the tricalcium aluminate. M. Le Chatelier assigns to it the formula $2(AlFe)_2O_3$, $3CaO$. He was able to produce synthetically a compound answering to this formula, and found it to possess the optical characteristics and the ready fusibility of the similar substance present in cement. This material is slowly acted upon by water, and is but little changed during the setting process.

4. Small crystals having a very energetic action upon polarised light. These are by no means numerous, and undergo no change upon coming in contact with water. These are probably magnesium compounds, since M. Le Chatelier has ascertained that all very basic calcareous compounds are acted upon by water in contradistinction to those of magnesia.

The results of M. Le Chatelier's more recent work in this direction were published in the *Annales des Mines*, 1887, pp. 388 to 412. In addition to a microscopic examination of cement with water, both in the form of clinker and after setting and hardening in water, he prepared various silicates, aluminates, and ferrites of lime by heating mixtures of the pure materials. Generally, his conclusions are as follows :—

The mono-calcium silicate, $CaO,SiO_2$, is unacted upon by water, and can, therefore, if present, contribute nothing to the hardening of cement.

The di-calcium silicate, $2CaO,SiO_2$, obtained by heating lime and silica, forms while hot a hard compact mass, which disintegrates and falls to powder while cooling. To the presence of this silicate the spontaneous disintegration of clinker when taken hot from the kiln is attributed.

The tri-calcium silicate, $3CaO,SiO_2$, is the one to which the hardening of Portland cement is due. This cannot be prepared by direct fusion of its constituents, but may be produced indirectly by fusing lime with a silicate.

The three aluminates, $CaO,Al_2O_3$, $2CaO,Al_2O_3$, $3CaO,Al_2O_3$, all set with water, and it is to their presence that the initial setting of cement, as distinguished from its ultimate hardening, is due.

The ferrites corresponding to the aluminates, in which the alumina is replaced by ferric oxide, slake on the addition of water and do not set.

On these results Le Chatelier based the formula we have already given in Chapter VIII. for calculating the proportion of lime to silica and alumina taken together in Portland cement, any magnesia present being considered as equivalent to lime.

**The Work of Tornebohm.**—We owe to Tornebohm, a Swedish investigator, who worked both with ordinary Portland and synthetic clinker from pure materials, a classification of the crystalline constituents as observed in thin sections.* He named the various substances alite, belite, celite, and felite. He was able to show that the amount of alite present is in direct proportion to the lime content of the cement, and that increase in the amount of iron augments the observed amount of celite. Clifford Richardson considers that alite is a solid solution of tri-calcium aluminate in tri-calcic silicate, and that celite is a solid solution of di-calcic aluminate in di-calcic silicate, the latter being more or less stained with iron. Belite may possibly be the calcium di-silicate, as it is found mainly in cement deficient in lime, and felite is thought to be another form of the same silicate which is known to assume two types. It is to the existence of one type of this silicate that the so-called dusting of cements can be traced. It passes at ordinary temperatures into an unstable condition with increase of volume, and the crystals composing the mass break up and give rise to the formation of a grey powder. It is frequently observed that felite is entirely absent.

**Messrs. S. B. and W. B. Newberry's Experiments on the Constitution of Hydraulic Cements.**—The results of these experiments were communicated to the New York section of the Society of Chemical Industry.† Working by synthesis with pure materials in an extremely fine state of division, very perfect mixtures of known composition were made of carbonate of lime with silica, alumina, oxide of iron, and magnesia respectively, which were burned in a Fletcher gas furnace with gasoline gas. A quantity of about 300 grammes of the mixture was taken for each experiment, the resulting products being ground and gauged with water; the hardening properties were then noted, and the soundness or constancy of volume was determined by the hot water test. Messrs. Newberry obtained the tri-calcium silicate, $3CaO,SiO_2$, by direct union of lime and silica which Le Chatelier failed to produce in this way. They also found that the tri-calcium aluminate, $3CaO,Al_2O_3$, when powdered and mixed with water, cracked after setting, and entirely disintegrated when placed in water. The general conclusions arrived at by them were as follows :—

1. " The essential constituents of Portland cement are tri-calcium silicate with varying proportions of di-calcium aluminate. This composition may, therefore, be expressed by the formula $X(3CaO,SiO_2) + Y(2CaO,Al_2O_3)$. From this formula it may be calculated that the correct proportion of lime, by weight, in Portland cement, is 2·8 times the silica *plus* 1·1 times the alumina."

2. " Iron oxide combines with lime at a high temperature, and acts like alumina in promoting the combination of silica and lime. For practical

* *Ueber die Petrographie des Portlandzements.* Stockholm, 1897.
† *Journ. Soc. of Chem. Ind.*, vol. xvi., 1897, pp. 887 to 894.

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purposes, however, the presence of iron oxide in a clay need not be considered in calculating the proportion of lime required."

3. " Alkalies, so far as indicated by the behaviour of soda, are of no value in promoting the combination of lime and silica, and probably play no part in the formation of cement."

4. " Magnesia, though possessing marked hydraulic properties when ignited alone, yields no hydraulic products when heated with silica, alumina, or clay, and probably plays no part in the formation of cement. It is incapable of replacing lime in cement mixtures, the composition of which should be calculated on the basis of the lime only, without regard to the magnesia present."

**Rankin's Researches.**—The most important recent researches on the constitution, setting, and hardening of Portland cement have been made in the laboratory of the United States Bureau of Standards by Messrs. P. H. Bates, A. J. Phillips, and A. A. Klein, whose work will be referred to later in this chapter, and in the Geophysical Laboratory at Washington by George A. Rankin, from one of whose papers * we give the following abstract :—

" For the purpose of the research described in this paper, an investigation of all the possible compounds of lime, alumina, and silica was made, this involving about 1,000 different mixtures of the three oxides and about 7,000 heat treatments and microscopical examinations of the resultant products. Each mixture, which was made of pure meterials, was alternately fused and ground to a fine powder with the object of obtaining a perfectly homogeneous product. The fusions were made in an electric furnace, the temperature of which was carefully controlled and measured. The resultant material was made the subject of a complete optical study. This enabled the crystalline phases present at temperatures, ranging from that at which fusion begins to that at which the charge is completely fused, to be determined. The melting temperature and optical characteristics of all compounds of lime, alumina, and silica were thus obtained."

" Microscopical examination of commercial Portland cement clinker shows it to be made up largely (over 90 per cent.) of the three compounds, $2CaO.SiO_2$, $3CaO.SiO_2$, and $3CaO.Al_2O_3$. It would appear, therefore, that the value of Portland cement as a cementing material when mixed with water is largely due to one or more of these compounds. Before taking up the cementing value of each of these compounds, however, let us consider their formation when Portland cement is burned.

" For this purpose let us follow the reactions which take place when a mixture whose composition is CaO (as $CaCO_3$) 68·4 per cent., $Al_2O_3$ 8·0 per cent., and $SiO_2$ 23·6 per cent. is slowly heated. This mixture made up only

* *Journal of the Franklin Institute*, 1916, pp. 747-784. Papers presented at a meeting of the Section of Physics and Chemistry. March 2nd, 1916.

of the pure oxides, lime, alumina, and silica, when properly burned, will produce a good Portland cement. When such a mixture is heated the first change is the evolution of the $CO_2$; the lime then unites with the other components to form the compounds $5CaO.3Al_2O_3$ and $2CaO.SiO_2$ (both of which form readily), probably in the order named, since the former has a lower melting-point than the latter; subsequently these two compounds unite in part with more lime, and the compounds $3CaO.Al_2O_3$ and $3CaO.SiO_2$ appear. This formation of the last two compounds—a process which goes on very slowly in mixtures of their own composition—is materially facilitated by the circumstance that in the ternary mixtures a portion of the charge has already melted and promotes reaction by acting as a flux or solvent. The temperature at which this flux first appears is 1,335° C., the eutectic temperature for the three compounds, $2CaO.SiO_2$, $5CaO.3Al_2O_3$, and $3CaO.Al_2O_3$. As the temperature of burning gradually rises above 1,335°, the relative amount of flux increases and the rate of formation of $3CaO.Al_2O_3$ and $3CaO.SiO_2$ increases correspondingly. At a temperature somewhat above 1,335°, the compound $5CaO.3Al_2O_3$ is complete. The substances present as crystals at this stage are $3CaO.SiO_2$, $3CaO.Al_2O_3$, $2CaO.SiO_2$, and free CaO. Of these, the $3CaO.SiO_2$ is rapidly increasing in amount, due to combination of $2CaO.SiO_2$ with CaO, while the amounts of solid $2CaO.SiO_2$, CaO, and $3CaO.Al_2O_3$ are all decreasing, the $2CaO.SiO_2$ partially by combination with CaO and partially by dissolving along with $3CaO.Al_2O_3$ in the flux. As the temperature is raised still further the amount of flux (liquid) increases and the rate of combination of $CaO.SiO_2$ to form $3CaO.SiO_2$ increases. But it is not necessary to raise the temperature until the charge is completely melted, as normal cement clinker is obtained at temperatures much below complete melting; in other words, the necessary reactions will go to completion below the temperature required for complete melting. The rapidity with which the reactions go to completion is governed by the temperature, and by the amount of flux formed at that temperature. The requisite amount of flux, in turn, depends upon the fineness of the raw materials, since the finer these materials are ground the more readily the components will combine. For finely-ground raw materials of the above composition, consisting only of $CaO,Al_2O_3$ and $SiO_2$, a temperature of about 1,650° C. is required for burning. At this temperature the clinker would be about 30 per cent. melted and 70 per cent. solid crystalline material, a proportion of flux which would admit of the necessary reactions going to completion in a reasonable time. The charge will always completely crystallise on cooling; the percentage composition (based on actual data) of the clinker thus obtained would be approximately $3CaO.SiO_2$ 45 per cent., $2CaO.SiO_2$ 35 per cent., and $3CaO.Al_2O_3$ 20 per cent. The melting temperature of the flux necessary for the production of the clinker is materially lowered by the presence of small amounts of impurities; that

the trifling quantities of $Fe_2O_3$, MgO, etc., in commercial cement actually have this effect is shown by the fact that the temperature required for burning is about 1,425° C."

From the results of his work, Rankin draws the following conclusions :—

" The value of Portland cement depends upon the fact that when finely powdered and mixed with water it forms a hard mass; and the strength and permanence of this mass depend upon the constituents of the cement. The major constituents are tricalcic silicate, dicalcic silicate, and tricalcic aluminate. Of these constituents, the compound tricalcic silicate is the one which hardens and develops the greatest strength within a reasonable time. This most important constituent, which is the one formed with the greatest difficulty, makes up only about 30 to 35 per cent. of an average normal Portland cement. It may be said, therefore, that the essential process for the manufacture of Portland cement is the formation of this compound, and that any improvement in this process yielding an increased percentage of tricalcic silicate will increase the cementing value of Portland cement."

**The Work of Bates and Klein.**—This work * is based on the assumption that the principal constituents of Portland cement are tricalcium aluminate, $3CaO.Al_2O_3$, tricalcium silicate, $3CaO.SiO_2$, and the beta form of dicalcium silicate, $2CaO.SiO_2$, and references are made to previous researches that support this view. We have already mentioned that there are two types of the last-named silicate, which are distinguished as the non-dusting or beta form, $\beta 2CaO.SiO_2$, and the dusting or gamma form, $\gamma 2CaO.SiO_2$. The latter is not desired in cement.

In the present investigation each of these compounds was prepared in the pure state and tested for tensile strength at the end of 24 hours, 7 days, and 4, 13, 26, and 52 weeks, and the amount of hydration at the end of each of these periods was determined by both chemical and microscopical methods.

The most important conclusions from the results of the experiments are as follows :—

" At the early periods the constituents of Portland cement of normal composition and manufacture, in the order of their strength-conferring properties, are—tricalcium silicate, tricalcium aluminate, and dicalcium silicate.

" At periods beyond 28 days the dicalcium silicate gains sufficient strength to place it almost on an equality with the tricalcium silicate.

" Tricalcium silicate of the purity used in this investigation (90 per cent. $3CaO.SiO_2$ in one case and 95 per cent. in the other) has all the important properties of Portland cement, especially those of the ' rate of setting ' and strength developed.

" Dicalcium silicate, such as used in this investigation, sets too slowly

* Technologic Paper of the U.S. Bureau of Standards, No. 78, 1917.

and attains strength too slowly to be of any commercial value when used alone.

" Tricalcium aluminate alone, as used in this investigation, sets too rapidly and attains too little strength to be of any commercial value as a hydraulic cementing material.

" Tricalcium aluminate, when used to replace about 19 per cent. of the dicalcium silicate (which is approximately the amount of aluminate present in Portland cement) adds somewhat to the strength of the latter at the later periods.

" Tricalcium aluminate, when used to replace about 19 per cent. of tricalcium silicate, did not add to the strength of the latter, showing rather a slight tendency to decrease it.

" Tricalcium aluminate, when used to replace about 19 per cent. of a mixture of equal parts dicalcium and tricalcium silicate, increased the strength at 24 hours and 7 days, but decreased it at the later periods.

" It appears that the composition of Portland cement should be along lines which would not produce a great preponderance of either silicate. The ideal cement should possibly have an excess of the dicalcium silicate, which would give a not too dense hydrated material, gaining strength at later periods.   A lesser amount of tricalcium silicate would furnish the desired early strength and also overcome the excessive porosity of the dicalcium silicate.

" It is possible to make a cement that will have the properties of Portland cement by grinding together the previously separately burned constituents in approximately the amounts in which they exist in Portland cement.

" The function of tricalcium aluminate in the finished cement is somewhat problematical.   A cement with less than 1 per cent. of alumina has all the properties of Portland cement.   Such a cement is, however, not a commercial possibility from the manufacturing standpoint, on account of the temperatures and amount of burning involved.   To state, however, that the aluminate in the finished cement is of the nature of a diluent or inert material would be drawing a conclusion which, while justified by the present investigation, requires further confirmatory work.

" The actual products of the hydration are those noted by Klein and Phillips." *

**The Crystalline Theory of Setting and Hardening.**—During the setting and hardening of cement certain definite reactions ensue, as regards which two distinct opinions are held, some authorities considering the action as one of crystallisation, others that its nature is colloidal.   The opinion that has been most often quoted with respect to the theory of the setting of cement regarded as a process of crystallisation is that of M. Le Chatelier.

* Tech. Paper, No. 43, this Bureau.

In his thesis for his doctor's degree in 1887,* and in a communication to the Faraday Society in 1918,† he maintains that the hardening of cements takes place as follows :—

" The anhydrous compounds of cements, not being in chemical equilibrium when in contact with water, are more soluble than the same hydrated compounds. For this reason they give rise to the formation of a supersaturated solution, from which the hydrated compound may rapidly crystallise. The liquid, being no longer saturated, can redissolve more of the anhydrous compounds, and the whole mass can thus crystallise progressively by passing through a stage of transitory dissolution in a limited volume of water, which, at any given moment, cannot maintain in solution more than a small portion of the total mass of salts present. The crystals which are deposited from the supersaturated solutions always appear in the shape of extremely elongated needles, which have the tendency to group themselves in spherolites about certain centres of crystallisation. The entanglement of all these crystals is the only cause of the solidity of the mass. They become welded with one another when the reciprocal orientation is suitable ; they adhere by simple contact, as do all solid bodies when really resting upon one another. Finally, friction at the points of contact, even in the absence of all adhesion, suffices to produce a great strength of mechanical resistance, such as is found in all tissues and fabrics whose solidity has no other origin. The finer and the more elongated the crystals, the more numerous the points of contact, and the greater the frictional resistance. The greater the area of contact the more developed the adhesion. The progressive growth of the crystal dimensions by the mechanism which I have suggested increases the part played by adhesion, while diminishing that due to friction. A material built up of very wide strips could be very solid if the strips were glued together at their contact surfaces."

The general line of argument adopted by M. Le Chatelier is based to some extent on the facts he had ascertained from a study of the behaviour of plaster of Paris when exposed to the action of water. He found in this case that the mechanism of the crystallisation of plaster in the act of setting was as follows :—

The calcined plaster stone becomes hydrated upon contact with the water used for gauging and yields a solution which speedily enables the hydrated sulphate to crystallise out, and the solution then becomes capable of dissolving a further quantity of dehydrated sulphate. This phenomenon goes on until the complete hydration and crystallisation of the mass. He contends, therefore, that in the case of hydraulic mortars it may be shown that

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* *Recherches Experimentales sur la Constitution des Mortiers Hydrauliques.* Paris, 1887. Second Edition with some Additional Papers. Dunod, Paris. 1904. Translation into English by Joseph Lathrop Mack, M'Graw Publishing Company, New York. 1905.
  † *Transactions of the Faraday Society,* vol. xiv., p. 13. 1918.

the crystallisation which accompanies the setting process results from the different degrees of solubility of the bodies in the act of hydration and those which are formed at this stage of setting, the former being in a condition of unstable equilibrium and only able to exist momentarily.

**The Colloidal Theory of Setting and Hardening.**—Coming now to the reactions relied upon by those who maintain that the setting of cements is due to the action upon substances in the mass which give rise to colloidal products, we may consider the views of Dr. Michaelis,* which he first propounded in 1893, reading a paper on the same subject before the Association of German Portland Cement Manufacturers in 1907. In this, he stated that the formation of a gelatinous substance or colloid was the only essential feature of the hardening of hydraulic cements, and that whenever water acted upon silicates saturated with lime, such as occur in Portland cement, such colloids were formed and hardened, any excess of lime crystallising as calcium hydrate. Iron oxide, and to some extent alumina, act in a similar manner, but they are not essential constituents of hydraulic cement, lime, silica, and water being sufficient. As proof of this, he refers to some tests made by himself 33 years previously with pure hydrated calcium silicate. This, with 9 parts of standard sand, gave a tensile strength after 14 days of 33·9 kilos. per square centimetre, after 60 days 42·5 kilos., and after 120 days 53·4 kilos., equal to 481·4, 603·5, and 758·3 lbs. per square inch. The crystalloids he considered increased the strength in the earlier stages of hardening, but later acted detrimentally; he admits, however, that hardening is always more or less accompanied by crystallisation.

**Researches of A. A. Klein and A. J. Phillips.†**—A description of these is best given in the words of the authors of the paper :—

" This laboratory has verified the work of the Geophysical Laboratory, and determined the compounds which are actually present in Portland-cement clinker. With the constitution of cement thus established, it was thought advisable to take up the study of the effect of various amounts of water and steam at atmospheric and higher pressures on the individual compounds of cement and on Portland cement itself.

" The work consisted of the preparation of the constituent binary compounds, their hydration on microscope slides with an excess of water, their hydration in a cylinder with steam according to the method proposed by Bied, their hydration in the autoclave with steam at various temperatures and pressures, and the hydration of specimens moulded with quantities of water approximating those used in normal consistency mixtures; all

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* Dr. Michaelis concluded a long paper by saying that the day had dawned on which the phases of hydraulic hardening, for the elucidation of which they had long laboured, would be made clear. He has not lived to see the end of this day, as he died in 1911 as the result of an accident in the 71st year of his age.

† Technologic Paper of the U.S. Bureau of Standards, No. 43, 1914.

products thus formed being examined· with the photographic microscope to determine the changes taking place.

"The treated products were the three aluminates, monocalcium aluminate ($CaO.Al_2O_3$), 5 : 3 calcium aluminate ($5CaO.3Al_2O_3$), and tricalcium aluminate ($3CaO.Al_2O_3$) ; four silicates, calcium metasilicate ($CaO.SiO_2$), gamma-calcium orthosilicate ($\gamma 2CaOSiO_2$), beta-calcium orthosilicate ($\beta 2CaO.SiO_2$), and tricalcium silicate ($3CaO.SiO_2$) ; free lime burned at different temperatures, a high silica cement, a low silica cement, a high iron cement, and a high magnesia cement. In addition to the above two white cements containing different percentages of water due to aeration were studied."

"In no case was it possible to secure a homogeneous product by one burning in the furnace. At least two burnings with intermediate grindings were necessary. This must be borne in mind in view of the comparisons which are made with the results of other investigators of this problem, since, with few exceptions, they made no reburnings and no petrographical examinations. Consequently it is doubtful whether their products were homogeneous and have the desired constitution."

The general conclusions drawn from the results of the research, as regards the hydration of Portland cement are as follows :—

"The hydration of cements is brought about by the formation of amorphous hydrated tricalcium aluminate with or without amorphous alumina, the aluminate later crystallising. At the same time sulphoaluminate crystals are formed, and low-burned or finely ground lime is hydrated. The formation of the above compounds begins within a short time after the cement is gauged. The next compound to react is tricalcium silicate. Its hydration may begin within 24 hours, and it is generally completed within 7 days. Between 7 and 28 days the amorphous aluminate commences to crystallise and beta-orthosilicate begins to hydrate. Although the latter is the chief constituent of the American Portland cements, it is the least reactive compound. The early strength (24 hours) of cements is probably due to the hydration of free lime and the aluminates. The increase in strength between 24 hours and 7 days depends upon the hydration of tricalcium silicate, although the further hydration of aluminates may contribute somewhat. The increase between 7 and 28 days is due to the hydration of beta-calcium orthosilicate, but here are encountered opposing forces, in the hydration of any high-burned free lime present and in the crystallisation of the aluminate. It is to this hydration that the falling off in strength between 7 and 28 days of very high-burned high-limed cements is due, whereas the decrease shown by the high alumina cements is due to the crystallisation of the aluminate. Finally, the iron in the cement is resistive to hydration, and does not form any definite crystalline hydration products, but occurs as a rust-like material."

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**Dr. Rosenhain's Theory of Setting and Hardening.**—Dr. Rosenhain has made an important contribution to the theory of the setting of cements * by likening certain stages of the process to what takes place during solidification of metals from a state of fusion. He compares the setting of plaster or cement to this action, and points out that in metals we have " a liquid setting into a strong hard solid owing to the formation of an aggregate of coherent crystals, instead of merely a heap of loose crystals, lying one upon another." He goes on to ask, " What is the mechanism by which crystals in such an aggregate adhere to one another? I think that we can dismiss at once the idea of mere frictional adhesion, due to any sort of interlocking. Frictional adhesion cannot account for the fact that, even in crystalline aggregates made up of equi-axed crystals, the intercrystalline cohesion is generally considerably stronger than the cohesion between the crystals themselves, so that, when the aggregate is forcibly broken, fraction occurs across the crystals and not along the crystal boundaries." He, therefore, puts forward the " hypothesis that the adhesion of crystals in metals is due to the presence between them of a film of amorphous material," and he shows that this explanation tends to support the probability of the " amorphous cement " theory. We may regard the cement as consisting, at one stage, of solid grains or crystals lying surrounded by a liquid solution of certain constituents. This liquid then undergoes solidification, as the result of the removal of water—either by percolation or chemical action, such as the hydration of some of the solid material present. If the film of liquid is thick enough, this solidification may take place by crystallisation, but if it is very thin it may—by analogy with the phenomena in metals—congeal in an amorphous condition. It is these amorphous films or layers which give to the whole mass its great stiffness and strength. He concludes, " We have here a theory which has proved useful and fruitful in explaining the setting of metals, and it may perhaps prove applicable to the analogous phenomena met with in the setting of cement and other crystalline aggregates."

* *Transactions of the Faraday Society*, vol. xiv., Pt. I., p. 54.

# CHAPTER XIX.

## THE EMPLOYMENT OF SLAGS FOR CEMENT-MAKING.

**Slags sometimes used for Adulteration.**—The days have now gone by, we may hope, when slags of all kinds are regarded with suspicion by cement users, owing to their occasional employment for the adulteration of Portland cement. It cannot be denied that for this purpose certain varieties of iron slag were extremely well adapted, since they approximate so closely in colour, weight, and composition to the cement itself that their presence could be detected only with difficulty, even by means of delicate chemical tests.

**Nature of Slags used to mix with Cement.**—The slags used for fraudulent additions to cement were generally those which had a tendency to disintegrate on exposure to the atmosphere, and which go abroad—*i.e.*, crumble—naturally into a bulky gray powder, having at times an astonishing resemblance to Portland cement. The fact of this spontaneous disintegration would seem to argue that some change, either of a physical or chemical nature, took place in consequence of atmospheric action ; probably these varieties of basic slag were selected chiefly because a powder could be obtained from them by mere sifting, without the expense and trouble of grinding, which is no easy matter in the case of the dense inert slags.

**Dr. Michaelis on Slag Mixtures.**—It is necessary that we should here allude to the opinions of Dr. Michaelis with respect to these admixtures of slag, for he has proved that with selected slags, used ·even in such large quantities as 30 per cent., it is possible to add considerably to the tensile strength of cement, both when tested neat and with the usual quantity of normal sand. In his open letter of 1884, he claimed that it is to the advantage, both of the user and of the manufacturer, that these mixtures should be permitted.

**Some Slags unacted upon by Moisture or by the Atmosphere.**—Certain varieties of acid slag would seem to be very little affected by air or moisture, and remain for years on the spoil-banks with arises as sharp and clean as

they were upon the day when they were tipped. Doubtless it was the apparent inertness of these materials which led experimenters to form the opinion that it was impossible to use them in cement-making, for the great similarity in composition of some descriptions of blast furnace slag with the clinker of Portland cement must have frequently caused attention to be directed to this material, in order to find a possible use for it as a cement component.

### ANALYSIS OF VARIOUS SLAGS * FROM IRON WORKS.

| Locality. | Silica. | Alumina. | Lime. | Iron Alkalies, Sulphur, &c. |
|---|---|---|---|---|
| 1. Staffordshire, . . . | 41·99 | 23·27 | 31·62 | 3·21 |
| 2. South Wales, . . . | 42·84 | 28·84 | 26·13 | 2·11 |
| 3. ,, . . . | 32·30 | 15·70 | 44·80 | 7·20 |
| 4. Yorkshire, . . . | 39·47 | 23·66 | 32·12 | 4·75 |
| 5. Lancashire, . . . | 33·49 | 10·12 | 46·97 | 8 54 |
| 6. Staffordshire, . . . | 49·05 | 10·84 | 34·33 | 5·78 |
| 7. Warwickshire, . . . | 41·30 | 16·20 | 40·80 | 2 70 |
| 8. ,, . . . | 36·30 | 13·86 | 30·49 | 9·76 |
| 9. Scotland, . . . | 32·10 | 24·28 | 35·43 | 8·10 |
| 10. Nottinghamshire, . . | 32·18 | 31·50 | 33·05 | 3·27 |
| 11. Lancashire, . . . | 38·68 | 13·13 | 45·82 | 2·37 |
| 12. Cumberland, . . . | 34·00 | 15·10 | 47·20 | 3·70 |
| 13. Derbyshire, . . . | 39·24 | 23·04 | 32·06 | 5·66 |
| 14. ,, . . . | 40·00 | 11·50 | 40·60 | 7·90 |
| 15. Lincolnshire, . . . | 32·86 | 21·88 | 40·34 | 6·12 |
| 16. ,, . . . | 31·37 | 19·69 | 40·23 | 8·71 |
| 17. Northamptonshire, . . | 39·06 | 21·54 | 37·16 | 2·24 |
| 18 North Wales, . . . | 31·28 | 12·41 | 46·10 | 10·21 |
| 19. Newcastle, . . . | 26·37 | 14·42 | 48·84 | 10·07 |
| 20. ,, . . . | 34·15 | 16·68 | 43·39 | 5·78 |
| 21. ,, . . . | 31·05 | 23·15 | 36·51 | 9·29 |
| 22. Cleveland, . . . . | 32·15 | 17·53 | 45·50 | 4·82 |
| 23. ,, . . . . | 35·45 | 21·55 | 33·70 | 9·30 |
| 24. ,, . . . . | 29·89 | 26·13 | 34·35 | 8·63 |
| 25. ,, . . . . | 30·98 | 28·03 | 33·33 | 7·60 |

**Slags produced at Extreme Temperatures.**—It must here be remembered, however, that the temperature at which slag is produced is much in excess of that needed to prepare Portland cement clinker, and, moreover, that in the case of the clinker too high a temperature in the kiln, resulting in complete fusion of the mass, leads to the formation of a blue-black glassy substance (slag), which, in consequence of its vitrification, is usually considered to be of little practical use for cement. The analogy of the two processes would again deter the investigator from further attempts to employ slag in cement-making.

* A great number of these are of no use for cement making.

**Admixture with Lime in Blast Furnace.**—Certain inventors have not been deterred by the high temperature of the blast furnace, and have at-tempted to prepare a suitable slag by the use of such proportions of limestone as would produce a slag having a composition resembling that of cement clinker in the furnace itself, but this process does not lend itself well to the iron manufacture, though a somewhat similar plan of manufacturing Portland cement has in recent years become very popular in Germany and in America.

**Composition of Blast-Furnace Slags.**—A glance at the table on the previous page will show that many iron slags contain all the essential ingredients of Port-land cement, though in none of them are they present in the same proportions as those selected by the cement maker. In almost every case there is a marked deficiency of lime, and nearly all the attempts made to utilise slag have involved the addition of lime in some form or other to the slag in a finely-divided state.

**Uniformity in Composition of Slag.**—The quality of the slag produced at any one works, where the same description of iron is being manufactured from ore of uniform type, varies within very narrow limits, as will be seen from the appended table, which gives the average analyses of a series of years expressed in percentages of the chief constituents :—

|  | 1888 to 1890. | 1893. | 1895. | 1899. |
|---|---|---|---|---|
| Silica, . . . . | 35·20 | 34·50 | 34·23 | 35·40 |
| Alumina, . . . | 10·02 | 10·90 | 10·28 | 10·45 |
| Ferric oxide, . . | 0·21 | 0·18 | 0·33 | } 0·91 |
| Ferrous oxide, . . | 0·55 | 0·64 | 0·64 | |
| Manganous oxide, . | 0·30 | 0·46 | trace. | 0·37 |
| Calcium oxide, . . | 47·10 | 47·44 | 48·26 | 46·74 |
| Sulphate of lime, . . | 1·56 | 1·44 | 1·87 | 1·72 |
| Sulphite of lime, . . | 2·17 | 1·99 | 2·07 | 1·81 |
| Magnesia, . . . | 1·20 | 1·36 | 1·13 | 1·20 |
| Alkalies (not determined). | ... | ... | ... | ... |
|  | 98·31 | 98·91 | 98·81 | 98·60 |

In certain works where the slags are rich in manganese it is possible to produce cements which may contain as much as 2 per cent. of this oxide, and these would tend to impart a brownish tint to the finished product.

**Some Former Attempts to employ Slags for Cement-Making.**—We cannot here afford sufficient space to do more than glance at a few of the various directions in which the problem of slag utilisation for cement production has been approached. Some have considered that by heating the requisite quantity of lime with the powdered slag a partial combination between the silica compounds and the added lime might be effected, and considerable success has been obtained by roasting processes on these lines in Germany

and in the United States. Others have endeavoured to bring about this combination in the wet way by grinding slag and lime together in a mortar-mill. It was thus that slag was employed for some time at Skinningrove Iron Works in the production of cement concrete for the construction of a sea-wall, etc. Lastly, slag has been used on a very extensive scale abroad, intimately mixed with slaked lime, without recourse either to heat or moisture.

**Slag Cement prepared from Slag Sand and Lime.**--As far back as 1862, Messrs. Lürmann & Langen, at Troisdorf, noticed that granulated slag was possessed of marked hydraulic properties, and in a report by Emil Langen on tests of this material, dated March 12th, 1862, it is stated :--" From these experiments it follows that the cement prepared from granulated blast-furnace slag, with a moderate addition of lime, provides a most valuable material for use either in air or water, and furnishes a cementing agent which takes an intermediate position between Rhenish trass and Portland cement, being in fact much superior to trass." Lürmann made practical use of this discovery, and in 1865 he was engaged in the manufacture of paving blocks and artificial stone. These blocks were made of concrete, consolidated in hand or steam presses, and allowed to set for six or eight weeks, and this industry attained to considerable importance. It was not, however, until about 1880 that so-called " slag cement " or " pozzolana cement " came into the market. Prof. Tetmajer, of Zurich, devoted much attention to the chemistry of these materials and to the treatment and manipulation of slag cements.

**Slag Cement as a Kiln Product.**--Considerable progress has been made both on the Continent and also in America in the production of cements from intimate admixtures of slag and lime, which, after having been calcined and clinkered in the kiln, are reduced to powder. This process is, as will be evident, in all respects analogous to the manufacture of Portland cement in the ordinary way, and renders the resulting material no longer liable to be classed as a pozzolana cement, as is the case with those which are simple admixtures of slag and quicklime. We believe that there are above ten or a dozen factories in Germany in which cements are prepared from slag on the following lines :- Slag sand, produced in the usual way from the slag derived either from grey or white pig irons, is dried, and ground in tube-mills to an impalpable powder. It is also freed from a certain amount of metallic iron by a powerful magnet. Limestone is likewise ground separately in a similar way, and the two powders are then carefully mixed in the proper proportions to yield a suitable cement compound. This is done in an automatic weigher and mixer. The mixture is subsequently moistened with water and pressed into blocks or bricks, which are dried and burnt in cement-kilns with interstratified fuel ; in fact, all the final stages of the manufacture exactly resemble those employed for producing Portland cement in the

ordinary way. Cements prepared in this manner from slag will stand all the tests to which Portland cement is commonly subjected, and when mixed with normal sand they yield surprisingly good results. A characteristic feature of all the slag cements, and one which differentiates them from the true Portland, is that all cements of the former type are comparatively poor in lime; the percentage varying from 54 to 60 per cent., while, in the case of the true Portland, the lime content ranges from 60 to 65 per cent. With less lime than 60 per cent. ordinary Portland is, as we have seen, apt to become quick-setting and poor in strength.

Two plants in the United States, the one in Pittsburg and the other in Chicago, likewise produce cement from slag by calcining in a similar way a mixture of compact limestone and granulated slag. It has been suggested that cements thus prepared should in all cases rank as true Portland cement, but that cements made from a mixture of slag sand and slaked lime, when these substances do not undergo any subsequent roasting process, should be classed as slag cements.

We may briefly describe the works of the Universal Portland Cement Co., of Buffington, Indiana, as typical of an American slag cement manufactory. The raw materials used are granulated blast-furnace slag and calcite limestone. The slag bin has a capacity of 4,400 tons, while the stone bin will contain 10,500 tons. These bins are placed under the raw material trestle and discharge direct into the raw material building, which is 288 feet long by 190 feet wide. The slag is dried in rotary driers and then conveyed to preliminary grinding mills, which reduce it to a fineness passing a 20-mesh screen. The limestone is also crushed, dried, and ground to the same fineness as the slag, and both materials are raised into hoppers, in which the correct proportions of each substance are adjusted by weight. The mixed ingredients then pass into tube-mills, in which they are ground to an extremely fine powder, and the mixture is calcined to clinker in 12 rotary kilns, each 140 feet long by 10 feet in diameter. The fuel is coal dust. The clinker is taken from the kilns into the clinker storage, which is 804 feet long by 100 feet wide, where it is handled electrically by cranes with grab buckets. The finishing mill is 306 feet long by 110 feet wide, and consists of four units, each of 4,000 barrels capacity, the daily output being thus 16,000 barrels. The grinding takes place in tube-mills, and the clinker is crushed between rolls before entering the mills. The annual production of Portland cement from this works and the other plants owned by the company is set down at twelve million barrels.

**Production of Slag Cement.**—It has been estimated that no less than forty factories were engaged a few years back in the production of slag cement, ten of these being situated in France and twelve in Germany, but several of these works have since been closed. A recent writer asserts that there are nine plants in the United States making slag cement. Of these,

two, as above stated, employ a roasting process.  The cement made without firing is very light both in colour and weight, while slag cements, which have undergone the roasting process, are rather darker in colour than ordinary Portland.  Slag cements are better adapted for use in water, or even in sea-water, than for purposes where they will be exposed only to the air; and, according to Le Chatelier, the alumina present in cement of this type does not undergo decomposition caused by the action of the sulphate of magnesia contained in sea water in consequence of the relative abundance of metallic oxides which they contain.

**Passow's Slag Cement.**—A patent was secured in 1901 by Dr. Passow for the manufacture of cement by blowing air into liquid slag issuing from the blast furnace, whereby it is granulated, and needs no further treatment except reduction to an impalpable powder.  It is claimed that by this process the silicate is partially decomposed, and that the following reactions take place :—

$SiO_2 2CaO$ yields $SiO_2 CaO + CaO$ and a certain amount of $SiO_2 + 2CaO$. We have thus mixtures of the di-calcium silicate with the monosilicate and free lime and silica, enough of the former being set free to render the addition of more lime unnecessary.  Only very basic slag from grey foundry pig can be used for this process, but it can be carried out practically, and if Portland cement can be produced in this very simple way, it would bid fair to revolutionise the manufacture.

**Process of Messrs. Bosse & Wolters.**—A successful process of making a cement resembling Portland cement from slag is that patented by Messrs. Bosse & Wolters.  Their invention consists in the selection of suitable slags, which are mechanically reduced to an extremely fine powder, and amalgamated in a machine of simple construction with a proportion of slaked lime.  In the ordinary process 25 parts of slaked lime are added to 75 parts of powdered slag.  The secret of success lies in the extremely fine grinding and the perfect amalgamation of the slag and lime.  In carrying out the manufacture, the slag, as it issues from the furnace, is run into water, giving rise to the formation of so-called " slag sand."  This material was patented many years ago by Mr. Charles Wood, of Middlesbrough.  It is found that when the molten slag falls into water it behaves much in the same way that glass does when used to produce Prince Rupert's drops, it flies into countless sharp fragments, resembling sand, the individual portions, as they fall, take the form of a porous pumice-like mass, which is very friable and capable of being easily crushed into powder.  Slag sand produced in this way has, however, certain disadvantages for the after processes to which it is subjected; it is, moreover, extremely retentive of water, and difficult to dry.

**Collos' Process.**—Much attention has from time to time been directed to the patents of H. Colloseus, and to his improvements in the manufacture of slag cement.  He has claimed, at various periods, the treatment of the

molten slag, as it issues from the blast furnace, with aqueous solutions of salts of calcium, aluminium, sodium, potassium, barium, and also iron compounds dissolved in water. He has likewise devised special apparatus for carrying out the addition of these solutions to the hot slag, and proposes to employ spray. He states that the water is at once vapourised, and the dissolved salts are dispersed in a finely divided state through the mass. He makes use also of milk of lime, in stated quantities, for addition to certain slags which are poor in lime, and by these additions he is able to produce from slags an iron Portland cement of good quality and high tensile strength. He specifies also the use of iron salts in solution to improve the hydraulic properties of the compound. He points out that by suitable additions of milk of lime it is possible to produce from selected slag a substance resembling trass and having similar qualities. The following analysis of Collos' cement may be cited—specific gravity 3·010.

| | |
|---|---:|
| Insoluble residue, | 1·30 |
| Silica, | 23·10 |
| Iron oxide (FeO), | 1·30 |
| Alumina, | 17·27 |
| Manganous oxide, | ·63 |
| Lime, | 43·53 |
| Calcium sulphide, | 4·97 |
| Calcium sulphate, | 1·40 |
| Magnesia, | 4·63 |
| Water, | ·75 |
| Carbonic acid, | ·25 |
| | 99·13 |

**Process of Mr. Snelus.**—Mr. G. J. Snelus, F.R.S., has described a process of making cement from slag, in which the moisture is expelled from the granulated slag by calcining it in a furnace, and he states that in the course of this process a notable quantity of sulphur, which is always present in slags as calcium sulphide, is gradually oxidised to calcium sulphate, accompanied by the evolution of sulphuretted hydrogen. The calcium sulphate, if present in moderation, beyond as we have seen tending to render the cement slow in its set, has no injurious action. The process of Mr. Snelus, which he has perfected, in conjunction with Mr. J. Gibb, does not involve the use of additional lime beyond that originally present in the slag. The following results in pounds per square inch were obtained on testing three samples of this cement neat :—

| | 7 days old. | 28 days old. | 3 months old. |
|---|---|---|---|
| No. 1 | 420 | 470 | 600 |
| No. 2. | 370 | 560 | 650 |
| No. 3. | 390 | 530 | 720 |

We are not in possession of full details respecting the process of manufacture, nor have we an analysis of this cement, but Mr. Snelus stated in 1890 at the Society of Arts, London, that 100 tons of slag were being used weekly for this purpose.

**Mode in which the Slag Sand is Prepared.**—There can be no doubt, however, that the act of forming the slag sand in the manner above described has a considerable influence on the behaviour of the material in the presence of lime, for it is found that when slag is allowed to cool slowly in the ordinary way, and is then reduced by mechanical means to a fine powder, it no longer possesses equivalent hydraulic properties in conjunction with the added lime. It is, therefore, probable that the rapid cooling or " chilling " has some physical effect upon the ultimate molecules of the slag, causing them to assume a state in which they can more readily undergo chemical action. At the time of entering the water, and in the fierce ebullition which then takes place, there is, moreover, undoubtedly a certain amount of chemical action, for with the steam an appreciable volume of sulphuretted hydrogen gas is given off, due probably to the decomposition of the calcium sulphide present in the slag.

**Mode of Manufacturing Slag Cement.**—In preparing the cement under Messrs. Bosse & Wolters' specification, the slag sand is first thoroughly dried, and to 3 parts by weight of the dry slag sand 1 part of dry slaked lime is added in the homogeniser, which consists of a drum or cylinder ; this may be of various sizes, the interior circumference is lined with fluted cast-iron plates, and in this drum are placed a number of chilled iron or steel balls, about 1 inch or $1\frac{1}{2}$ inches in diameter. The mixture of slag and lime is passed into the drum through a hollow trunnion, by means of a worm feeding apparatus, and when a full charge has been added, the aperture is closed and the cylinder is caused to rotate slowly on its axis, with the result that the contents are, by the constant collisions of the revolving balls on the fluted lining, pounded and reduced to an extremely fine state of subdivision, and at the same time most perfectly mixed. When this operation has been continued for an hour, or for such time as may be found sufficient to grind the mixture thoroughly, a door in the outer lining is opened and the contents, in the course of a few revolutions, are ejected through a shoot into a bag or barrel ; the balls being retained by a coarse grating. The charge thus produced is now ready for the market, not requiring to be sifted or handled in any way.

**Manufacture is Economical.**—It will be seen from this description that the manufacture of slag cement is an extremely simple one, needing but little skilled labour and a relatively cheap plant. The area needed for the works is small, and a French writer, who has had considerable experience, states that the entire cost of works and plant for an annual output of 6,000 tons (say 20 tons of cement per diem) is under £6,000, in which estimate he

improvement is chiefly noticeable when the cement is tested with sand. It will at once be seen that the finer the grinding the greater is the power of uniting together the sand particles, as the action of a cement depends to a very great extent upon the amount of surface that it will cover.

**Properties of Slag Cement.**—We may now glance at the properties of the slag cement, which differs to a marked degree from Portland, for while the specific gravity of a good sample of the latter would average about 3·10, that of slag cement never exceeds 2·75, the slag from which it is made having a specific gravity of about 3·00, and that of slaked lime being only 2·08, the diminished density being no doubt partly due to the porosity of the slag sand. A cubic foot of the slag cement weighs, therefore, about 75 lbs., or the bushel would weigh 90 lbs., being thus about 20 per cent. lighter than Portland cement. Slag cements are essentially of the slow-setting type, rarely taking less than five hours for this purpose. They distinguish themselves from Portland chiefly from the fact that they reach their greatest degree of induration in less than twelve months ; in fact, in many cases they show but little improvement after the first month. They test extremely well with sand, owing to the extremely fine grinding, and there is less difference between the tests of the neat cement and that with 3 parts of sand than is observed in the case of most samples of Portland cement. Owing to the slowness of the set, they are ill-adapted for plastering and stucco, and they do not produce so hard a surface as that obtained by the use of Portland.

These cements behaved admirably under all the volumetric tests, and they will stand perfectly unchanged the various steaming and boiling processes for accelerated set. The German manufacturers have adopted for them the generic name of " Iron Portland Cement," and a powerful association has been formed by the makers of this material, entitled the " Verein Deutsche Eisenportlandzement-Werke," with a testing station and laboratory at Dusseldorf, Breite-Strass 27.

**Iron Portland Cement.**—After long controversy in Germany, and protracted experiments, the so-called " Iron Portland Cement " was recognised by a ministerial commission in 1908 as equivalent to Portland cement, and this material has taken definite rank in that country as a building material since the date in question. It is asserted that about one-third of the cement used for public works in Germany is of the nature of iron Portland cement. In the year before the war, the slag available in that country for cement manufacture was estimated to amount to little less than 19 million tons. Considerable quantities of slags are also added to Portland cement, in a finely ground state, to improve the quality, and the specification for iron Portland cement authorises a mixture of 70 per cent. of Portland with 30 per cent. of powdered slag, to be sold as "Iron Portland Cement." With respect to the special user of this material, it is claimed that iron Portland

cement is superior to ordinary Portland cement when employed in sea water, and the reason given is that the calcic hydrate formed in the setting process, which in the case of the iron Portland cement goes at once to the silica of the slags, is in the ordinary Portland cement the substance exposed to the attack of the magnesia salts, and sometimes brings about the ultimate failure of the concrete.

**Slag Cement can be Stored with Impunity.**—Slag cement compares favourably with other similar materials when stored for long periods. If freely exposed to the air, the available lime gradually unites with carbonic acid, and this action is relatively much more rapid than is the case with Portland : thus, in four days a thin layer of slag cement gained about 5 per cent. of carbonic acid, the amount of this acid taken up in the same time by a similar sample of Portland cement was only 1 per cent. The slag cement does not, however, greatly deteriorate in tensile strength by prolonged storage, as the following experiment tends to prove :—A sample of the cement was tested with sand, and gave, at seven days, 254 lbs., and at twenty-eight days 340 lbs. per square inch, with 3 parts of normal sand. After being kept for fifteen months, and similarly tested, the figures were 243 lbs. at seven days, and 321 lbs. at twenty-eight days, showing, therefore, a loss in strength of less than 5 per cent. Slag cement yields such a fat rich mortar that it lends itself peculiarly well for works under water. Used for sea-walls, as has been done at Skinningrove, near Saltburn-on-the-Sea, it rapidly attains great hardness, and makes excellent work.

**The Chemistry of Slag Cement.**—The chemistry of the cement action in the case of this material is somewhat obscure, and tends to subvert certain of the theories which have been put forward to explain the induration of Portland cement. Before considering the question further we may glance at the following analyses :—

|  | Portland Cement. | Slag Cement. |
|---|---|---|
| Lime (CaO), | 61·07 | 39·68 |
| Silica, | 21·70 | 24·34 |
| Alumina, | 8·60 | 18·74 |
| Protoxide of iron, | ... | 0·27 |
|   ,,   manganese, | ... | 0·23 |
| Peroxide of iron, | 2·25 | 0·14 |
| Magnesia, | 1·17 | 6·59 |
| Potash, | 0·75 | 0·28 |
| Soda, | 0·42 | 0·44 |
| Sulphur, | ... | 0·93 |
| Sulphuric acid, | 1·93 | 0·25 |
| Carbonic acid, | 0·80 | 4·07* |
| Water and loss, | 1·26 | 4·70 |
| Total, | 99·95 | 100·66 |

* Carbonate of lime equal to lime 2·28, carbonic acid 1·79.

Here we have in the first column a sample of Portland cement of average composition, and in the second an analysis of slag cement. If the carbonate of lime in the latter analysis is separately set down as lime and carbonic acid we have in the slag cement $39 \cdot 68 + 2 \cdot 28 = 41 \cdot 96$ per cent. of lime, as compared with $61 \cdot 07$ per cent. in the Portland cement, though probably the $6 \cdot 59$ per cent. of magnesia in the former may be regarded as ranking with the lime.

**Proportion of Lime and Magnesia to Acids.**—If we take the total percentage of lime and magnesia in both cements, equal to $48 \cdot 55$ in the slag cement and $62 \cdot 24$ in the Portland, we find that the equation of total lime divided by silica $+$ alumina is roughly $\frac{3}{2}$ in the slag cement, as compared with $\frac{2}{1}$ in the Portland. This latter equation is fairly representative of the average composition of all good specimens of Portland cement, and we should at first sight consider it quite impossible that a cement having the formula of $\frac{3}{2}$ would give good results.

**Composition of Slag Cement throws some Doubt on Chemistry of Portland.** —We are in fact compelled to reconsider certain of our theories respecting the action of the silicates and the relative proportion of lime required to obtain cementitious properties. It is probable that in the case of slag cement, at the very high temperature attained in the blast furnace (that of complete fusion), compound silicates of lime and alumina, together with small quantities of metallic and alkaline silicates, are produced, which, when taken alone, are almost entirely inert. That is to say, that when they are reduced mechanically to a fine state of subdivision there is but little tendency among the particles to form fresh compounds in the presence of water. The energetic action of hydraulic cements of the Portland type is largely due, as we have elsewhere shown, to the formation of hydrated aluminates and silicates of lime, which rapidly solidify the water used in making the mortar, and are said to set. In nearly all specimens of Portland there is undoubtedly a considerable margin of lime which readily gives up the alumina or the silica, with which it is combined, on the addition of water. It has frequently been described as " free lime," or even as " uncombined lime," though from recent experiments it is, as we have seen, very doubtful whether any good sample of hydrated Portland cement, or even of hydrated slag cement, contains much lime which can be spoken of as free lime. Some of this lime may, however, either have been present in the original mixture in excess of the requirements of the alumina or the silicic acid, or it may have become mechanically entangled in or coated with the vitreous, or semi-vitreous, silicates formed in the kiln.

**Free Lime in Portland Cement.**—It is difficult to estimate the exact proportion of this available lime, but we are warranted by what takes place in the case of slag cements to consider that the amount is considerably larger than chemists have hitherto thought possible. When Portland has been

steamed or thoroughly " purged," and the whole of the available lime has been set free and hydrated, the cement loses its energy of set, and is rendered much safer and more reliable in its action. If, as Le Chatelier supposes, the chief active constituent of Portland cement is the tri-calcium silicate, and if on treatment with water this silicate is, as he asserts, decomposed into two molecules of crystalline hydrate and one molecule of hydrated mono-silicate of lime ; or if, as Meyer claims, on purely theoretical grounds, it splits up into two molecules of calcium hydrate and one of anhydrous mono-silicate, under either assumption there is a considerable margin of lime becoming capable of hydration. What takes place, when water is added to the mixture of pulverised slag and hydrate of lime in the slag cement, must be a partial decomposition of the sparingly soluble silicates of the slag and a mutual reaction between them and the lime, which latter in itself (being previously fully hydrated) is incapable of being further acted upon by water. The slag contains but little free lime, as it is but slightly attacked by acids, but there is no doubt a slow and gradual decomposition of the silicates and aluminates and the other bases present in the slag, and a reaction ensues between these silicates and the calcium hydrate, leading to the formation of fresh compounds of lime, silica, and alumina, which are not only themselves capable of induration, but possess also the power of uniting very considerable quantities of aggregates in the form of mortar and concrete.

**Excess of Lime in Portland Cement.**—If this theory could be regarded as accurate, it will be seen that it follows as a necessary consequence, either that in Portland cement a superfluity of lime is present (to the extent of something approaching 20 per cent.), or that in the slag cement, possibly in consequence of the high temperature of calcination, different combinations of the lime and other substances are obtained, which would, however, appear to be quite as stable and permanent as those prepared at a much lower temperature in the cement kiln. This fact has led both Dr. Michaelis and Prof. Zulkowski to suggest that it would be better to melt the cement clinker into slag in suitable furnaces rather than to stop short at the present stage of incipient fusion.

**Theory of Cement Action needs Revision.**—We cannot, however, escape the conviction that the behaviour of the mechanical mixture of silicates and calcium hydrate forming the slag cement throws considerable doubt upon those theories of cement action which imply that in Portland cement the induration is brought about by the hydration of ready formed aluminates and silicates, or that certain silicates of lime, alumina, iron, and the alkalies, produced in the kiln by the action of heat, are in the presence of water recombined or transformed into hydrated double silicates, since it is evident that in the slag cement, when produced by cold mixing, notable quantities of hitherto uncombined lime are united to the silicates of alumina or other

bases present in the slag. The exact nature of the chemical changes which take place has, we regret to say, not yet been satisfactorily explained, though numerous attempts have, as we have seen, been made to account for these reactions.

**Other Considerations involved besides Chemical Ones.**—That other considerations besides purely chemical ones influence the behaviour of the slag is, however, shown by the following samples of slag sand, which when analysed gave almost identical results, but which, when treated in the same way and mixed with precisely the same amount of lime, gave widely different results. The composition of the slags was as follows :—

| Ingredients. | A. | B. |
|---|---|---|
| Silica, . . . . | 24·10 | 23·22 |
| Alumina, . . . . . | 16·30 | 15·61 |
| Lime, . . . . . | 46·53 | 47·10 |
| Oxide of iron, . . . . | 0·93 | 0·78 |
| Soda, potash, &c., . . . | 5·04 | 5·56 |
| Carbonic acid, . . . . | 0·65 | 0·85 |
| Moisture, . . . . | 6·45 | 6·88 |
| Totals, . | 100·00 | 100·00 |

Tested with sand in the same way, the tensile strength of the cements produced by the addition of lime was—

| 1 Cement to 3 Sand. | | | |
|---|---|---|---|
| A. | | B. | |
| 7 days. | 28 days. | 7 days. | 28 days. |
| Lbs. | Lbs. | Lbs. | Lbs. |
| 326 | 431 | 150 | 208 |

showing a difference of over 50 per cent.

**German Tests of Slag Cement.**—In order to show the behaviour of this cement when tested, the authors consider that the following details of the examination of a sample made and sealed up in the presence of one of them and forwarded to the Imperial German Testing Station at Berlin in December, 1886, may be of interest, and it will serve also to show the very careful and searching manner in which such trials are conducted, and speaks well for the qualities of this material. The investigation is extracted from the *Proceedings of the Institution of Civil Engineers.*

INVESTIGATION OF SAMPLE OF SLAG CEMENT CARRIED OUT BY THE ROYAL
TESTING-ESTABLISHMENT FOR BUILDING MATERIALS AT BERLIN.

Results of the examination of a parcel of cement forwarded on the
3rd December, 1886, marked " Sample of Cement," without further par-
ticulars as to locality.  The tests were commenced on the 9th December,
1886, under the rotation number Spec. XVI., No. 4,764.
As a mean of three observations in each case :—

|  | Kilogrammes. | Lbs. per Cubic Foot. |
|---|---|---|
| 1 litre of the cement lightly filled = . . . | 1·042 | 65 |
| „        „      shaken down = . . . | 1·611 | 100·5 |
| „    normal sand = . . . . . | 1·640 | 102·3 |

The normal sand was obtained by the selection of the finest possible
quartz sand, which was washed and dried.  From it were removed all the
coarse particles rejected by a sieve of 60 meshes to the square centimetre,
and only the particles subsequently retained on a sieve of 120 meshes per
square centimetre were employed.
.The production of a suitable mortar needed 40 per cent. of water, 500
grammes of the cement being used.  A slightly stiffer mortar required
36 per cent. of water ; the temperature of the cement and the water being
the same, and equal to that of the atmosphere of the laboratory, the rise
of temperature on mixture was 0·7° Centigrade.  It was made up into pats
on glass, and set in 2¾ hours, the average temperature throughout the experi-
ment being 22·5° Centigrade.
Tested with the sieve, the following results were obtained :—

5,000 meshes per square centimetre, 14·0 per cent. residue.
900   „        „        „      5·0   „        „
600   „        „        „      1·0   „        „
324   „        „        „      0·5   „        „
180   „        „        „      0·0   „        „

The tests for expansion and contraction were carried out by means of
ten pats of neat cement, made up on glass and roofing-tile, and trowelled
to a thin edge.  The pats remained twenty-four hours in air, and were then
placed in water.  They kept perfectly true and sharp-edged, and were free
from cracks.  There was no expansion or contraction, and the cement adhered
to the glass.  When broken it presented a close even-grained and uniform
fracture.
The briquettes employed to ascertain the tensile and compressive strength
were made up on December 10, 1886, as follows :—
(a) The neat cement was mixed with 16½ per cent. of water.

(b) The sand briquettes were made of 1 part by weight of cement, 3 parts by weight of normal sand, and 7½ per cent. of water. The mixture was beaten into metal moulds placed on glass plates in the usual way.

The temperature of the air was 22·5° Centigrade.
,, ,, ,, water was 16·2° Centigrade.
The moisture of the air was 68 per cent.

The tests set the first day in air, covered up with writing paper to avoid too rapid desiccation; the remainder of the time they were in water. Taken from the water and tested they gave the following results :—

| Mixture. | Closeness after Filling. | TENSION. | | | | Closeness after Filling. | COMPRESSION. | | | | Proportion of Tensile to Compressive Strength. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Tensile Strength after | | | | | Compressive Strength after | | | | | |
| | | 7 days. | | 28 days. | | | 7 days. | | 28 days. | | 7 days. | 28 days. |
| | | German. | English. | German. | English. | | German. | English. | German. | English. | | |
| | | Kils. per sq. cm. | Lbs per sq. in. | Kil's per sq. cm. | Lbs. per sq. in. | | Kils. per sq cm | Lbs per sq. in. | Kils. per sq. cm. | Lbs. per sq. in. | | |
| Neat. 1 to 0 | 2·113 | 45·50 | 646·0 | 48·65 | 692·0 | ... | ... | ... | ... | ... | ... | ... |
| Sand. 1 to 3 | 2·261 | 30·03 | 428·0 | 35·78 | 510·0 | 2·262 | 237·3 | 3,376 | 300·1 | 4,269 | 1 to 7·902 | 1 to 8·337 |

NEAT CEMENT (TENSION).

| No. | 7 days. | | 28 days. | | Remarks. |
|---|---|---|---|---|---|
| | German. | English. | German. | English. | |
| | Kils. per sq. cm. | Lbs. per sq. inch. | Kils. per sq. cm. | Lbs. per sq. inch. | |
| 1 | 44·25 | 629 | 48·25 | 686 | Made on metal plates, with 16½ per cent. of water. |
| 2 | 45·50 | 642 | 45·75 | 651 | |
| 3 | 43·25 | 615 | 53·00 | 754 | |
| 4 | 48·00 | 683 | 49·00 | 697 | |
| 5 | 44·00 | 625 | 48·00 | 683 | |
| 6 | 46·50 | 653 | 48·50 | 694 | |
| 7 | 45·75 | 651 | 48·25 | 686 | |
| 8 | 44·25 | 629 | 52·50 | 746 | |
| 9 | 48·00 | 683 | 46·25 | 657 | |
| 10 | 45·50 | 647 | 47·00 | 668 | |
| Total, | 455·00 | 6,457 | 486·50 | 6,922 | |
| Average, | 45·50 | 646 | 48·65 | 692 | |

## 1 Part Cement and 3 Parts Sand (Tension).

| No. | 7 days. | | 28 days. | | Remarks. |
|---|---|---|---|---|---|
| | German. | English. | German. | English. | |
| | Kilos. per sq. cm. | Lbs. per sq. inch. | Kilos. per sq. cm. | Lbs. per sq. inch. | |
| 1 | 31·50 | 448 | 38·25 | 544 | Made on non- |
| 2 | 30·00 | 427 | 35·00 | 498 | absorbent plates, |
| 3 | 28·50 | 405 | 36·50 | 518 | with 7½ per cent. |
| 4 | 31·50 | 448 | 37·75 | 536 | of water. |
| 5 | 29·00 | 412 | 35·50 | 505 | |
| 6 | 31·00 | 440 | 34·50 | 490 | |
| 7 | 30·50 | 433 | 35·75 | 508 | |
| 8 | 31·50 | 448 | 34·50 | 505 | |
| 9 | 27·25 | 387 | 33·50 | 476 | |
| 10 | 30·00 | 430 | 36·50 | 519 | |
| Total, | 300·75 | 4,278 | 357·75 | 5,099 | |
| Average, | 30·07 | 428 | 35·78 | 510 | |

The briquettes were kept for the first day in the air, and the remaining time in water.

## 1 Part Cement and 3 Parts Sand (Compression).

| No. | 7 days. | | 28 days. | | Remarks. |
|---|---|---|---|---|---|
| | German. | English. | German. | English. | |
| | Kilos. per sq. cm. | Lbs. per sq. inch. | Kilos. per sq. cm. | Lbs. per sq. inch. | |
| 1 | 229·6 | ... | 287·8 | ... | Made on non- |
| 2 | 252·0 | .. | 292·3 | ... | absorbent plates, |
| 3 | 237·4 | ... | 305·8 | .. | mixed with 7½ |
| 4 | 235·2 | ... | 303·5 | ... | per cent. of |
| 5 | 233·0 | ... | 292·3 | ... | water. |
| 6 | 234·1 | ... | 304·6 | ... | |
| 7 | 229·6 | ... | 291·2 | ... | |
| 8 | 246·4 | ... | 315·8 | ... | |
| 9 | 230·7 | ... | 292·3 | ... | |
| 10 | 245·3 | ... | 315·8 | ... | |
| Total, | 2373·3 | ... | 3001·4 | ... | |
| Average, | 237·3 | 3,376 | 300·1 | 4,269 | |

# CHAPTER XX.

## SCOTT'S CEMENT, SELENITIC CEMENT, CEMENTS PRODUCED FROM SEWAGE SLUDGE AND THE REFUSE FROM ALKALI WORKS, AND SIDERO CEMENT.

CONTENTS.—Discovery of Scott's Cement.—Faraday's Opinion on the Theory of this Cement—First Patent for Scott's Cement—Influence of Sulphur on Lime—Selenitic Cement—Theory of this Cement Action—Tests of Selenitic Cement—Graham Smith on Sulphates—Cement from Sewage Sludge—Alumina Cement—Cement from Alkali Waste—Composition of the Cement—Cement from Caustic Soda Waste —Sidero Cement.

**Discovery of Scott's Cement.**—In the course of some attempts to produce an artificial hydraulic lime by calcining lumps of chalk in a common fire-place, about the year 1854, General (at that time Captain) Scott, R.E., found to his surprise that the calcined lime would not go abroad or crumble to dust in the usual way in water. Tested with acid, the lime was found to be properly burned, but it had lost its avidity for water. Captain Scott was thoroughly puzzled by this result, and he consulted Dr. Faraday in his difficulty.

**Faraday's Opinion on the Theory of this Cement.**—After careful consideration of the facts, that eminent chemist came to the conclusion that this change in the behaviour of the lime was due to the formation of some form of sub-carbonate of lime—a compound the existence of which previous investigators had suspected, and which was believed to confer new properties upon the calcined lime, the most important of these being the above mentioned failure to fall into powder when quenched or sprinkled with water.

**First Patent for Scott's Cement.**—So convinced was General Scott of the accuracy of this surmise that he was induced to patent the process provisionally in March, 1854, No. 735. In his specification he proposed to prepare a cement either by calcination, so applied as to drive off only a portion of the carbonic acid contained in chalk or limestone, leaving the substance in the state of sub-carbonate, or by subjecting ordinary quicklime or supercalcined lime to heat in the presence of carbonic acid, so as to bring it back to the state of a sub-carbonate. He also specified a third process of mixing quicklime and carbonate of lime in such proportions as to cause them to form, when properly treated, a sub-carbonate.

**Behaviour of Lime due to Sulphur in the Fuel.**—Subsequent experiments proved this invention to be founded on a misconception, and it was ultimately discovered that the change in the behaviour of the lime was due to the presence of small quantities of sulphate of lime, produced from the sulphur

are mechanically deposited over the molecules of lime owing to surface-attraction. The coating of sulphate retards the access of water to the lime ; it forms, if we may so style it, a temporary varnish, through which, however, owing to its solubility, the water speedily penetrates, and the molecules of lime then become hydrated, but this action is retarded to such an extent that the combination with water takes place gradually, without much evolution of heat, and with little or no perceptible increase of volume. The latter fact is proved by the much greater density of the selenitic hydrate than that of a hydrate formed in the ordinary way.

The paste formed by the selenitic process is sufficiently bulky to penetrate the interstices between the sand-grains and to bind together a large quantity of this sand into a mortar, though, of course, it is far less finely divided than the particles of fully slaked lime from which mortar is ordinarily made. The hydrate used for common mortar is, however, not really a binding agent in the true sense of the word at all.

**Sulphur has no Effect on Pure Limes.**—If pure lime is treated in this way with a soluble sulphate no retarding influence is exerted, for the hydration takes place instantaneously before the coating is formed ; it is only in the case of hydraulic limes, in which the combination with water is more gradual, that the coating of sulphate has time to form. Some interesting experiments by Mr. F. Schott, elucidating this theory, were published in Dinglers' *Polytechnische Journal*, in vol. clix., 1873, p. 30.

**Feebly Hydraulic Limes best adapted for Treatment.**—The selenitic process may be employed with advantage with all limes of a feebly hydraulic character, and it also greatly improves the eminently hydraulic limes of the lias formation. Limes of this kind, when made selenitic, will carry a largely increased volume of sand and give good results. Strong tough mortar and good plasterers' stuff may be produced from a mixture of 1 part of selenitic lime with from 4 to 6 parts of sand, and it is a matter of common experience that any given sample of lime when prepared by the selenitic process will give double the tensile strength with twice as much sand, as when slaked and mixed into mortar in the ordinary way.

**The Colour of Selenitic Cement.**—In consequence of the fact that the lime does not become slaked, when employed in accordance with General Scott's process, it retains its original colour, a warm buff, and the mortar is, of course, much more dense than one made from the hydrate. The power of binding together large volumes of sand is strikingly shown by the tests to which this material and the original Scott's cement have been at different times subjected.

**Improvement Effected by Selenitic Process.**—The improvement effected upon limes, when treated with a small percentage of plaster, as compared with the same materials when used in the ordinary way, is well seen in the following table, which gives some tests carried out at the New Law Courts,

under the late Mr. Street, R.A. They were made by Mr. A. W. Collinge, the Clerk of the Works. The resistances were arrived at by pulling asunder two bricks united crosswise, so as to give a joint having an area of 18¼ square inches. One month was allowed for setting. In every case the mortar was made in a mill, and the mean of three tests is indicated :—

| Material and mode of preparation. | Proportion of sand to lime. | Mean resistance in lbs. |
|---|---|---|
| Lias gray lime as common mortar, . . | 3 to 1 | 112 |
| ,, ,, selenitic ,, . . | 6 ,, 1 | 209⅔ |
| Barrow lime as common mortar, . . . | 3 ,, 1 | 125 |
| ,, ,, selenitic ,, . . . | 5 ,, 1 | 283⅔ |
| ,, ,, ,, ,, . . . | 6 ,, 1 | 196 |

**Tests of Selenitic Cement.**—From a large number of tests made by one of the authors to ascertain the strength of selenitic cement, as compared with Portland cement, the following have been selected because they clearly indicate the advantages of the selenitic treatment when carried out with suitable limes. The lias lime here used was that from Barrow-on-Soar, and the gray lime was from the Burham pits on the Medway. The whole of the samples were prepared by the late Mr. Hartley, who had a long experience in cement testing. The tests were in all cases made with ordinary stock bricks bedded across one another at right angles, giving a joint with an area of 20 square inches.

| Nature of Material. | Age in Days when Fractured. | Parts of Sand to 1 of Cement or Lime. | | | |
|---|---|---|---|---|---|
| | | 3 Sand. | 4 Sand. | 5 Sand. | 6 Sand. |
| Portland cement, . | 28 | ... | 463 | 325 | 313 |
| Barrow selenitic, . | 28 | 541 | 418 | 399 | 399 |
| Burham selenitic, . | 28 | 484 | 454 | 368 | 408 |
| Portland cement, . | 35 | ... | 520 | 433 | 309 |
| Barrow selenitic, . | 35 | 435 | 539 | 438 | 430 |
| Burham selenitic, . | 35 | 424 | 430 | 490 | 556 |

**Kirkaldy's Tests of Selenitic Cement.**—By far the most important series of tests of this material with which we are acquainted was carried out for the Selenitic Cement Company by Mr. D. Kirkaldy in 1872; these are here reproduced in tabulated form. He ascertained the resistance of selenitic .

cement exposed both to forces of tension and compression. In the former set of experiments he made use of test-briquettes having an area at the neck of 5 square inches, and also of bricks bedded crosswise, having a sectional area at the joint of 18·5 square inches. The blocks used for the tests in compression had a base area of 7·84 square inches. The test-briquettes of common lime mortar, when broken eight weeks after being made, showed a mean strength of 23·6 lbs. per square inch. Selenitic mortar, made from the same lime and with double the sand, attained in a similar time a strength of 83·0 lbs. per square inch. Blocks of common mortar crushed under a load of 121·7 lbs. per square inch, but when treated selenitically and used with twice the sand, the blocks withstood a load of 629·6 lbs. per square inch.

**Experiment in Slaking Lime Powder.**—The selenitic action is likened by Mr. Schott, to whose theories we have already alluded, to what takes place when dry, finely-powdered quicklime is tightly packed in a metal cylinder pierced with very minute perforations. If such a cylinder of lime is placed in water, which can then only reach the lime in very small quantities and very gradually, the lime is converted into a dense hydrate, which resembles in every way the hydrate formed by the selenitic process. This experiment would seem to confirm the accuracy of Mr. Schott's theory of the selenitic process.

**Mr. Graham Smith's Observations on Sulphates.**— It is much more difficult to understand the reason of the influence of sulphate of lime on slaked lime, as observed by Mr. Graham Smith, who, in a paper on " The Effect of Sulphates on Lime Mortar," has shown that calcium sulphate has a notable influence when mixed in certain proportions with slaked hydraulic limes. In 1870, while he was in charge of the various cements and mortars employed in the works in progress at the Liverpool Docks, he carried out a large number of experiments with Halkin lime from Flintshire, a variety of white lias with fair hydraulic properties.

The analysis of this limestone is as follows :—

ANALYSIS OF HALKIN MOUNTAIN LIMESTONE.

| Composition. | | Percentage. |
|---|---|---|
| Substances soluble in acids — 74·726 per cent. | Carbonate of lime, | 71·546 |
| | Carbonate of magnesia, | 1·348 |
| | Protocarbonate of iron, | 1·040 |
| | Sulphide of iron, | |
| | Alkalies, | 0·792 |
| Substances insoluble in acids— 25·274 per cent. | Silicic acid, | 20·068 |
| | Alumina, | 3·521 |
| | Sesquioxide of iron, &c., | 1·192 |
| | Water and carbonaceous matter, | 0·493 |
| Total, | | 100·000 |

The whole of the mortar used in the tests was mill-made, ground 30 minutes ; the proportions indicated are in all cases by volume. The briquettes were of the ordinary shape, $1\frac{1}{2}'' \times 1\frac{1}{2}''$, or $2\frac{1}{4}$ square inches in area. They were broken in a Michele lever cement-testing machine. Corresponding tests were made with bricks bedded crosswise on the flat, giving a joint of $4\frac{1}{4}'' \times 4\frac{1}{4}'' = 18$ square inches, and the results though similar were scarcely so favourable to the sulphate mortar as the briquette tests which we have appended.

**Common Slaked Lime Mortar Improved by Sulphates.**—It will be seen that with $4\frac{1}{2}$ per cent. of sulphate, even with double the volume of sand, the mortar was much stronger than when lime alone was employed. It is to be regretted that no results are given with other proportions of sulphate. This mortar was found not to be adapted for use under water. The explanation of the foregoing results is surrounded with many difficulties, as the chemical action is quite different from that of selenitic cement, in which the slaking action is controlled by this means. We must probably seek for the solution in connection with the silica and alumina compounds of the Halkin lime, and it would be interesting to ascertain the behaviour of other hydraulic limes treated in a similar way.

EXPERIMENTS WITH HALKIN LIME MORTAR WITH AND WITHOUT SULPHATE
OF LIME.

| DESCRIPTION OF MORTAR. | Lime. | Sand. | Ashes. | Mixed with Salt or Fresh Water. | Number of Lbs. required to Break by Tension Briquettes of $2\frac{1}{4}$ Square Inches.* | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | 21 Days. | 42 Days. | 84 Days. | 168 Days. |
| Ordinary mortar, . . . | 1 | 2 | $\frac{1}{4}$ | Fresh. | 60 | 130 | 153 | 248 |
| Do.    do.,    . . . | 1 | 2 | $\frac{1}{4}$ | Salt. | 47 | 74 | 134 | 147 |
| Do. with $4\frac{1}{2}$ per cent. plaster, | 1 | 2 | | Fresh. | 98 | 141 | 340 | 375 |
| Do.    do., | 1 | 2 | | Salt. | 67 | 183 | 232 | 387 |
| Do.    do., | 1 | 3 | No ashes used with the Sulphate. | Fresh. | 122 | 156 | 306 | 398 |
| Do.    do., | 1 | 3 | | Salt. | 140 | 210 | 376 | ... |
| Do.    do., | 1 | 4 | | Fresh. | 97 | 154 | 299 | 422 |
| Do.    do., | 1 | 4 | | Salt. | 100 | 190 | 401 | ... |
| Do.    do., | 1 | 5 | | Fresh. | 65 | 193 | 253 | 360 |
| Do.    do., | 1 | 5 | | Salt. | 70 | 232 | 312 | 320 |

* In all cases the average of three tests.

**Cement from Sewage Sludge.**—While treating of General Scott's cement, we must briefly allude to his proposals for the manufacture of cement from sewage sludge, a plan which was actually carried out upon a considerable scale at Birmingham, Burnley, Ealing, and several other towns, and one

which enables the authorities to dispose of their sewage sludge with profit and advantage. This invention was a development of the so-called "lime process" of sewage treatment. In accordance with this process, a small quantity of slaked lime (from 15 to 23 grains per gallon) in a fine state of subdivision is added to the sewage water, and as this substance becomes mixed with the water in the sewer it gives rise to a copious precipitate, consisting mainly of carbonate of lime, together with a little phosphate of lime. The sewage is then allowed to pass into tanks where the flow is arrested, and the precipitate slowly sinks to the bottom, and in so doing it entangles and carries down with it nearly all the suspended impurities, leaving the supernatant water thoroughly clarified, and in a fit condition to be discharged into rivers of large volume. The sewage sludge or mud which remains at the bottom of the tank, when this clear effluent has been drawn off, is dried either on hot floors or by mechanical pressure, or other suitable means, and when sufficiently dried it is burnt in down-draught kilns of special construction, with small quantities of interstratified fuel.

**Character of Sewage Cement.**—General Scott was able to produce in this way a cement which had approximately the composition of Portland cement, because the detritus and clayey matters washed from the surface of the roads, and the ash of the fæcal and other organic substances, always present in sewage water, furnished the amount of silica, alumina, and iron needed for the cement. In dry weather it became necessary in certain cases to add a small quantity of clay to the sewage water along with the lime ; this addition of clay aids in the clarification of the sewage, and need rarely exceed a few grains per gallon. This plan of dealing with sewage had manifest advantages, as it enabled municipal authorities to get rid of the sludge without expense, and lime is well-known to be the cheapest and best precipitating agent. It was found in practice that from 1 to 1½ tons of quick-lime were needed for the treatment of one million gallons of sewage water, or, say, for the daily volume of sewage produced by a population of 25,000 persons. If the cost of lime be taken at 15s. per ton, this implies a cost of 9d. per diem per thousand inhabitants. From each ton of lime used with sewage of average composition, there will result 30 tons of wet sludge or 3 tons of dry sludge. This sludge when calcined will yield about 1½ tons of cement. It will be evident that, after undergoing calcination, all noxious matters will have been completely destroyed, and this plan of disposing of town sewage has thus many important recommendations from the hygienic point of view.

**Difficulty of Drying Sewage Sludge.**—One of the chief drawbacks encountered in carrying out this process upon a commercial scale was that the resultant sludge was extremely retentive of water and difficult to dry. The raw materials were also more fusible than the ordinary slurry, composed of lime and clay, in consequence, no doubt, of the large admixture of organic matter derived from the excreta ; but we are of the opinion that

this process, if it were efficiently carried out with the appliances now available for burning and grinding, would be found a successful and economical plan of disposing of the sludge, which has always been one of the main obstacles encountered in dealing with town sewage by treatment with lime.

**Quality of Cement from Sewage Sludge.**—The quality of the cement made in this way will manifestly greatly depend upon the composition of the sewage water, and on the impurities present therein. By carrying out the calcination at a lower temperature, the sludge may be converted into hydraulic lime, or a lime suitable for agricultural use. It was found by experiment that, for each ton of lime introduced into the sewers, 45 bushels of good agricultural lime, valued by Dr. Voelcker at 1s. per bushel, were obtained. The cement made at Burnley, which was calcined at a high temperature, though it fluctuated somewhat widely in composition, owing to the varying quantities of detritus carried into the sewers during rainy weather, commanded a ready sale, and showed a fair degree of tensile strength. We believe that this valuable invention was somewhat in advance of its time, but that, with the present state of our knowledge of cement manufacture, it could be carried out with complete success, and would prove a means of overcoming many of the difficulties in defecating town sewage.

**Aluminous Cements.**—Though the compounds of lime and silica for the purpose of cement-making have received a large share of attention, the compounds of lime and alumina and the presence of aluminates in cements have been to some extent disregarded. Alumina has sometimes been considered as an objectionable element, when present in cements in too large a quantity, though it was known to be valuable as a flux. The general rule laid down by Eckel is that "the percentage of lime being constant, the clinkering temperature decreases with the silica alumina ratio, while the setting time and ultimate strength of the cement are in inverse proportions to the value of the ratio."

Many different compounds of lime with alumina have been identified, and it would appear from the researches of Sheppard and Rankin that these are seven in number, but they consider that only one of them—namely, $3CaOAl_2O_3$—occurs in Portland cement. It is, however, generally stated by writers on the chemistry of cements that the alumina in the cement, if present as a separate compound, was combined with two equivalents of lime, $2CaOAl_2O_3$, and this does not agree with the above theory.

Exhaustive researches on aluminates with a view to their employment for the improvement of lime mortars were made by Henry Spackman, of Philadelphia, who read a paper dealing with the subject before the Franklin Institute in February, 1909, and one in 1910 before the American Society for Testing Materials. He gave the results of much of his work, making especial reference to the action of calcium aluminates on lime mortar, which demonstrated that they increased its plasticity, rapidity of hardening, and sand-carrying properties.

There is little doubt from what has been observed concerning the action of alumina compounds that these substances act to some extent as energisers of cement action, and they may be added to lime, either subsequent to or before kiln treatment; in fact, at any time previous to use.  The most convenient method of employing them is to incorporate them with the lime to be used for mortar or plaster in the form of a dry hydrate, in which condition they can be handled and stored in the same manner as Portland cement, as they keep well.

A considerable trade has sprung up in America in the preparation of the so-called "Alca" plasters, which consist of an intimate mixture of slaked lime with about 15 per cent. of the aluminate of lime, prepared by burning together lime and alumina, and carefully grinding the calcined material.  Made in this way, the compounds of calcium hydrate with the aluminates of lime develop great hardness, and can be employed with excellent effect for plastering walls and ceilings, or as ordinary mortar; the strength in the latter case being quite four times as great as with common lime mortar made from lump lime in the usual way.

The aluminates can also be used with very satisfactory results in admixture with lime and substances like trass and pozzolana, for the production of hydraulic mortars.  The hardness and strength of lime-alumina mixtures can, in all cases, be much increased by the addition of finely divided silicious material or clay matter, and all mixtures of natural pozzolana material and lime mortars are much increased in strength by the addition of aluminates.  Many of the American makers of natural cements are, in fact, employing the "Alca" process to improve their materials.

During the time the experiments of Spackman were in progress, with the view of improving the common limes by the addition of aluminates, Jules Bied was experimenting in the laboratory of J. & A. Pavin de Lafarge, Le Teil, near Marseilles, with the object of producing cement that would resist the destructive action of sea water.  By fusing bauxite, a mineral that contains about 50 per cent. of alumina, 25 of iron, together with silica and other impurities, with limestone in a water-cooled blast furnace at a temperature of about 1,450° C. and grinding the product, he obtained cement differing widely in composition from Portland and other hydraulic cements, in that it contains more alumina and less lime, and with changed properties.

The most important sources of bauxite are in the South of France, in the North of Ireland, near Glenramel in County Antrim, and in Alabama, Georgia, and Arkansas in North America.  Details of the manufacture of the cement are not generally known.  At the present time it is made by three works in France and one in Switzerland.  The Swiss works and two of those in France use electric furnaces, obtaining current from hydro-electric plants.

The cement is known under various names—Ciment Fondu, Fused Cement, Lafarge Cement, Ciment Electrique, Electric Cement, Aluminous

Cement. The exact proportion of its constituents is not of so much importance as in the composition of Portland, and depends on the purity of the bauxite.

The percentage of lime is about equal to that of the alumina, and the chemical composition is approximately as follows :—

| | |
|---|---|
| Silica, . . . . . . . | 10 per cent. |
| Alumina, . . . . . . . | 40 ,, |
| Iron and iron oxide, . . . . . | 10 ,, |
| Lime, . . . . . . . | 40 ,, |

Ciment Fondu sets slowly, the final set occurring about eight hours after gauging. It then hardens rapidly with the evolution of considerable heat, and at the end of 24 hours its strength equals that of Portland at 28 days. This property renders it valuable for many purposes. It was used during the war for gun emplacements. Candlot gives an instance of a roadway constructed with it on a Saturday evening at Le Teil which carried a 5-ton tractor on Monday morning.

A portion of the roadway in Guilford Street, London, was recently laid with reinforced concrete made with this cement, and was hard and fit for traffic on the following day. It resists the action of both sea water and sulphate waters perfectly, but is at present more costly than Portland.

**Super Cement.**—Many substances are sold under various names to be added to cement concrete or mortar at the time of mixing, with the object of rendering it impervious to water. In super cement a material for effecting the same purpose is added in very small quantity to ordinary Portland cement while grinding, and it is claimed that this addition at the same time materially increases its strength. So treated it is resistant to water, oil, and petrol. In some tests by Messrs. Kirkaldy, a slab 1 inch in thickness, composed of 1 part of super cement and 1 of Thames-washed sand, withstood a water pressure of 300 lbs. per square inch gradually applied for 34 days. A similar slab tested with petrol resisted a pressure of 50 lbs. per square inch maintained for 67 days. In both instances the slabs were entirely unpenetrated.

**Cement from Alkali Waste.**—By means of certain patented processes Messrs. Chance are now enabled to extract from the alkali waste, resulting from the manufacture of soda on the Leblanc system, a very large part of the combined sulphur which was present as sulphate and polysulphides of calcium. This discovery may hereafter provide a mode of utilising these vast mounds of bye-products which now encumber the ground, and so sadly disfigure the vicinity of alkali works. In order to find some means of using the-lime after the sulphur has been extracted, it has been more than once proposed to employ this material in the manufacture of Portland cement, but the percentage of sulphur still remaining in the waste has hitherto rendered this out of the question. By introducing a slight modification

of the treatment, one of the authors has succeeded in producing Portland
cement from this material, and from a paper published by him in the *Journal
of the Society of Chemical Industry* of June 30th, 1892, we have extracted
the results of certain experiments made about that time with a sample of
alkali waste which had the following composition :—

| | |
|---|---:|
| Coke, | 2·492 |
| Sand, | 1·094 |
| Silica, | 1·156 |
| Alumina, | 0·926 |
| Ferrous sulphate, | 1·488 |
| ., sulphide, | 0·421 |
| Calcium carbonate, | 68·861 |
| ,, sulphate, | 4·735 |
| Magnesium carbonate, | 2·428 |
| Soda, | 0·962 |
| Water, | 15·714 |
| | 100·277 |

For reasons given below this material after being dried and ground
was mixed with a marly clay, containing 30 to 40 per cent. of carbonate
of lime, and a considerable excess of water, which was allowed to drain
off ; advantage being thus taken of the slight solubility of calcium sulphide.
The dried slurry thus produced was found after careful calcination to yield
a cement which stood high tests and gave good results when mixed with
sand. As this substance proved very fusible, considerable care was needed
in the burning, and the mixture with a clay rich in carbonate of lime was
rendered necessary to bring down the proportion of calcium sulphate in
the resultant cement.

**Composition of the Cement.**—The dried slurry was found to have the compo-
sition shown in Col. 1, and in Col. 2 we give the analysis of the cement :—

| | No. 1. | No. 2. |
|---|---:|---:|
| Coke, water, and organic matter, | 1·032 | ... |
| Sand, | 1·349 | 2·749 |
| Silica, | 12·220 | 18·215 |
| Ferrous oxide, | 3·427 | 6·563 |
| ,, sulphide, | 0·324 | ... |
| Alumina, | 4·993 | 8·048 |
| Calcium carbonate, | 71·002 | ... |
| ,, sulphate, | 2·455 | 5·006 |
| Lime, | ... | 56·682 |
| Magnesium carbonate, | 1·955 | ... |
| Magnesia,. | ... | 1·639 |
| Potash, | 0·671 | 0·654 |
| Soda, &c., | 0·772 | 0·779 |
| | 100·200 | 100·335 |

It was found in practice that if it is so far free from sulphur compounds as to give in the cement a quantity not exceeding 5 per cent. of calcium sulphate, alkali waste may, after treatment by the Chance process for the recovery of its sulphur, be successfully utilised for the manufacture of Portland cement. We learn, indeed, that Messrs. Chance have themselves established the manufacture of cement from their waste, upon a commercial scale, and that they are now producing considerable quantities of Portland cement of excellent quality from this material.

**Production of Cement from Caustic Soda Waste in America.**—In order to work up the waste arising in soda manufacture, the Michigan Alkali Company, using the ammonia soda process and producing about 110 tons of waste per diem, erected a plant in 1899, from the designs of Messrs. Lathbury and Spackman, to convert the bye-product into Portland cement. The residuum, which is pure white in colour and free from grit, is mixed with the bluish clay from the valley of the Detroit River. The following analysis shows the composition of the raw materials. Unlike the waste from Messrs. Chance's Works, the residuum from the ammonia soda process is practically free from calcic sulphate, but the percentage of magnesia was deemed to be excessive. The limestone at first used has, therefore, been discarded in favour of one with a much smaller quantity of magnesium carbonate, and the waste used as the lime ingredient now contains only about 1 per cent. of magnesia :—

WASTE.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Calcium carbonate, | . | . | . | . | . | 74·85 | } = 50·40 CaO. |
| Calcium hydrate, | . | . | . | . | . | 11·24 | |
| Magnesium carbonate, | . | . | . | . | . | 8·24 | } = 4·97 MgO. |
| Magnesium hydrate, | . | . | . | . | . | 1·52 | |
| Silica, | . | . | . | . | . | ·98 | |
| Oxides of iron and alumina, | . | . | . | . | 1·62 | |
| Sulphur, | . | . | . | . | . | ·06 | |
| Alkalies, | . | . | . | . | . | ·50 | |
| | Total, | . | . | . | . | 99·01 | |

CLAY.

| | | | | | | |
|---|---|---|---|---|---|---|
| Silica, | . | . | . | . | . | 46·81 |
| Oxides of iron and alumina, | . | . | . | . | 14·21 |
| Calcium carbonate, | . | . | . | . | 25·07 |
| Magnesium carbonate, | . | . | . | . | 7·58 |
| Sulphuric anhydride, | . | . | . | . | 1·18 |
| Alkalies, | . | . | . | . | . | 3·04 |
| | Total, | . | . | . | 97·89 |
| | Loss on ignition, | . | . | . | 15·74 |

Very special attention has been paid in the design of the works to so arrange the plant as to be as nearly automatic as possible, and to avoid

all resort to manual labour. The clay is first dried in rotary driers, and is then introduced in the requisite proportions into the liquid waste, and the mixture is pugged with additional water. The liquid slurry is then ground in tube-mills, so that 95 per cent. will pass a 200-mesh sieve. The slurry is pumped into rotary kilns, and burnt into clinker by coal dust mixed with air under pressure. The clinker at the discharge end of the kiln falls into a hopper-shaped concrete pit, whence it is raised by elevators into a specially-designed cooling bin. After final grinding in ball-mills and tube-mills, the cement is elevated and carried by an overhead conveyor into storage bins, from whence it passes to the packing machinery. The capacity of the plant is 450 barrels per diem.

**Sidero Cement.**—Dr. Michaëlis introduced a variety of cement, which he termed " sidero cement," in which clays rich in alumina are replaced by iron ores or ores of manganese, and even chrome ore tailings, and these are used in conjunction with chalk marl rich in silica. It was pointed out in 1875 by Michaëlis and Schott that the alumina in cement mixtures might be replaced by iron oxide, since the ferrite of lime and the manganite of lime harden just as well under water as the aluminate of lime, and Portland cement made under these conditions is no longer liable to the formation of the double salt, the silicate of lime and alumina. This crystallises with a relatively large percentage of water and with a considerable increase of volume, and owing to its high percentage of lime in combination with the alumina, it is peculiarly exposed to the attacks of the magnesium sulphate present in sea-water.

By the selection of suitable ingredients rich in iron or manganese, which are incorporated with chalk marl containing very little magnesia and alumina, but with a high percentage of active silica, Portland cement may be produced by the dry process and calcined in rotary kilns. The mixture is so made that from two to three equivalents of lime are added to one equivalent of the hydraulic factors, $SiO_2 + R_2O_3$.

The mixture must be burnt to a clinkering heat, but as the calcium ferrites sinter at a lower temperature than the ordinary Portland materials, the cost of fuel is less than under the old process. The sidero cement clinker varies in colour from brown-black to black, and when ground it produces a light brown or a chocolate-brown powder, or, if rich in manganese, the powder will be black-brown in colour. The specific gravity is higher than is the case with the ordinary Portland cements, and may run from 3·25 to 3·35, and may even reach 3·44; this is due to the large percentage of iron present.

The chemical composition of the ore cement is indicated by the analyses shown at top of next page : wherein one part by weight of the hydraulic factors (silica and oxide of iron and alumina) is combined with 1·890, 1·906, 1·970, and 1·800 parts of lime respectively.

|                           | A.       | B.      | C.              | D.      |
|---------------------------|----------|---------|-----------------|---------|
| Silica, . . . .           | 21·785   | 23·841  | 19·901          | 22·243  |
| Alumina, . . . .          | 4·431    | 2·852   | 3·548           | 1·602   |
| Oxide of iron, . . .      | 6·062 )  |         | ( 9·643 )       |         |
| Oxide of manganese, . .   | 1·814 )  | 8·269   | ( 0·150 )       | 11·138  |
| Lime, . . . .             | 64·476   | 62·830  | 65·557          | 62·416  |
| Sulphate of lime, . . .   | 0·888    | 1·239   | 0·602           | 0·995   |
| Magnesia, . . . .         | 0·291    | 0·554   | 0·658           | 1·174   |
| Potash and soda, ) Not    | ..       | ..      | ..              | ..      |
| Insoluble, ( determined.  | ..       | ..      | ..              | ..      |
|                           | 99·747   | 99·585  | 100·059         | 99·568  |

The cement is relatively slow in setting, probably owing to the absence of the energetic action of the aluminate of lime, when treated with water ; but after three days in water, the material attains a considerable degree of strength, and in the later stages of induration it even surpasses Portland cement in its resistance to crushing stress, which is in close accord with the density of the mortar.

Sidero cement perfectly withstands the action of sea water, and it is also unacted upon by soda, lime, magnesia, and by iron sulphate. It can be mixed with considerable quantities of gypsum without any sign of expansion or disintegration, and it may be used with good effect with ordinary Portland cement, to which it imparts an additional degree of hydraulicity, and by this means the brown colour of the original cement may be varied to any shade from light grey to dark brown.

The following figures indicate the resistance of the new cement to tensile and crushing stresses in lbs. per square inch. A and B are samples of neat cement, and C is cement mortar, with 3 parts of normal sand. Each result is the average of ten separate tests :—

| Age.     | A.       |              | B.       |              | C.       |              |
|----------|----------|--------------|----------|--------------|----------|--------------|
|          | Tension. | Compression. | Tension. | Compression. | Tension. | Compression. |
| 3 days,  | 414      | 5,600        | 415      | ...          | 143      | 1,657        |
| 7 ,,     | 714      | 11,243       | 700      | 10,714       | 207      | 3,114        |
| 28 ,,    | 794      | 14,885       | 857      | 15,500       | 371      | 3,428        |
| 90 ,,    | 905      | 16,285       | 943      | 16,057       | 457      | 5,915        |
| 1 year,  | 915      | 17,500       | 971      | 18,000       | 486      | 7,143        |
| 2 years, | 861      | 19,715       | 929      | 20,143       | 557      | 8,757        |

Tests which have been made with the sidero cement in sea water show scarcely any visible traces of attack, such as softening at the edges, blowing, or cracking, after exposure for two years, and it would appear that in this new material engineers have a reliable cement for marine constructions of all kinds.

# CHAPTER XXI.

## THE COMPOSITION OF MORTAR AND CONCRETE.

CONTENTS.—Definition of Mortar—Action of Sand—Sand Weakens Cohesion—Opinions of Early Writers—Proportion of Sand Added—Vicat and Pasley on the Use of Sand—Totten's Theory on Sand Addition—Size of Sand Grains—Scott on Proportion of Sand—Preparation of Mortar—Artificial Stone—Concrete—Armoured or Reinforced Concrete.

**Definition of Mortar.**—Mortar, as the term is commonly understood in this country, is applied to the mixture of lime or cement with water to form a plastic matrix for embedding or uniting together bricks or masonry. Such mortar invariably contains a certain proportion of sand. It was an opinion very widely entertained by the earlier writers on building construction that this sand had a beneficial effect on the mortar to which it was added, though we now know that there is no foundation for this belief.

**Action of Sand in Mortar.**—There are perhaps certain cases in which sand of a peculiar description and used in small quantities may tend to improve a sample of lime or cement, but such cases are quite the exception, for sand can only be regarded in the light of recent experiments as a diluent, or as tending to diminish the strength of any given specimen of lime or cement, and the only valid reason that can be urged for its use is the advantage gained in point of economy by the employment of a cheaper material. It has been, however, pointed out that, when exposed to compression in mortar joints, the influence of the hard particles of sand, if duly compacted, may be beneficial, owing to the increased power of resisting a crushing strain possessed by the hard particles of quartz, as compared with the friable or putty-like mass of a pure lime mortar or even of a stratum of cement.

**Properties of Mortar.**—Mortar suitable for ordinary buildings must have the consistency of a creamy paste, in order to work well under the trowel into the joints and interstices of the materials. It should have considerable power of adhesion, so as to retain the substance with which it is being used in position, and it should possess the power of rapidly indurating and of becoming in course of time as hard as the remainder of the structure, which it should bind together into a species of monolith. Moreover, it should be capable of resisting the attacks of the atmosphere, moisture, and the other destructive influences to which buildings are ordinarily exposed.

**Influence of Sand.**—It will be obvious, therefore, that, apart from the

qualities of the lime or cement, the sand which enters so largely into the composition of mortars of every description has an important function to fulfil, and though it does not increase the strength of the compound, its action upon the mortar should be carefully studied.

**Sand may Act in Four Different Ways.**—We may consider its probable effects under four heads. *First*, Respecting the cohesion of the particles of the cementing material. *Second*, The adhesion of the lime or cement to the surfaces of the sand grains. *Third*, The possibility of causing weak places, due to the occurrence of several particles of sand in contact without a sufficient supply of cementing material to envelope them and to fill up all the interstices ; *and lastly*, the increase of strength the sand may develop, in such cases in which the sand grains are stronger than the cementing material, in consequence of the line of fracture being longer than it would be if no sand particles were present to interrupt the direct passage of the fracture in one plane.

**Sand Tends to Weaken Cohesion of Mortar.**—Treating of these various points *seriatim*, we know from numerous tests, conducted by skilled observers, with every description of lime and cement, that the cohesion of the particles of mortar made from neat lime or cement is nearly always greater than that which is found to exist between the particles of the same cementing material when used with sand. If we regard the matter simply as one of cohesion or adhesion, though wide differences doubtless exist between the behaviour of various qualities of sand, whether the surface of the grains be rough or smooth, or whether the lime or cement be capable or incapable of exerting a chemical action upon them, the general effect of sand, which retains its position in the mass by the force of adhesion only, is to lessen the force of cohesion. The diminution of strength will be greater in the case of fine sand than it will be when coarse or large-grained sand is employed, and it will invariably be larger in direct proportion to the amount of sand we use. For in both these cases the surface to be covered with the cementing agent is enlarged. We substitute, in fact, a lesser force, that of adhesion, for a greater force, that of cohesion, the more sand we add. To the same extent, also, that we increase the amount of sand, we incur the risk of weak points from a deficiency of cementing material. The only benefit we can trace then to the employment of sand is the interposition of the sand grains into the direct path of fracture, which they tend to lengthen and increase, and in so far as these grains are stronger than the lime or cement we are using, they may improve the mortar.

**Sand does not, therefore, improve the Mortar.**—On the whole, the advantages of the sand do not counterbalance the sources of weakness introduced by it into the mortar, and practical experiments confirm the truth of these views. Mortar is, in fact, merely rendered cheaper by the employment of sand, but not in any sense improved by its use.

**Opinions of Early Writers on Sand in Mortars.**—From the time of Vitruvius onwards, all writers on the subject appear to have taken it for granted that a due admixture of sand must tend to improve the mortar. The earliest builders no doubt found that lime used alone, especially in the form of stucco, had a tendency to shrink and crack in drying, and that this failing could be corrected by the addition of a certain proportion of sand. Having once established this fact, we can well understand that it soon became a settled doctrine that the use of sand was a matter of necessity in the production of a good sample of mortar, but it is strange to find how greatly opinions have differed respecting the reasons for the beneficial effects of this addition, and respecting the proper proportion of sand to be employed.

**Proportion of Sand Added.**—Vitruvius asserts that " when the lime is slaked it is necessary to mix 3 parts of sand, if the sand is fossil (pit sand), with 1 part of lime ; and if the sand is river sand to add 2 parts of it to 1 of lime." He goes on to say that these are the best proportions to use for mortar, and he accounts for the hardening of the mixture somewhat ingeniously as follows :—-" The weight of the lime after calcination is diminished about one-third by the evaporation of the watery parts ; from this it results that the pores being empty they are better fitted than before to receive the admixture of sand, and to unite strongly with the blocks of stone to form solid masonry."

**Theories for Use of Sand.**—Many authorities ancient and modern follow Vitruvius and adopt his views ; some of them endeavour to invent equally fanciful theories to prove the advantages conferred by the sand. Thus Macquer states that " the particles of slaked lime adhere more closely to hard bodies than to each other, on account of the great quantity of water united to them, which prevents their coming so closely into contact as they do with sand or cement (pozzolana), for these substances by absorbing a portion of the water of the slaked lime facilitate the drying and adhesion." The amount of water absorbed by sand would be infinitesimally small, and this theory is manifestly incorrect, though it has some show of reason in its favour.

**Invariable Rule Established to Add Sand.**—It gradually became recognised as an established fact among builders that lime was capable of taking up a prescribed dose of sand (the amount assumed to be the correct proportion varied greatly), and it was not until Vicat and the careful experimenters of the French school, and our own countrymen, Smeaton and Pasley, began to conduct independent tests that the old faith in the efficacy of sand began to be shaken.

**Proper Proportion of Sand to be Used.**—In the matter of proportions there has been at all times a great difficulty in deciding exactly what was really intended by writers upon this subject. Some authorities made their mixtures by weight, some by volume, some used lump lime, and others

used slaked lime, so that no two results are strictly comparative. The views of Smeaton on the employment of sand are sound and good. He states that: "The use of sand in mortar, so far as I have been able to observe, is two-fold—1st, to render the composition harder; and 2nd, to increase it in quantity by a material that in most situations is of far less expense, bulk for bulk, than lime. As there is no apparent change in the sand by the admixture of the lime, the sand seems only to render the composition harder, by itself being a harder body; for the best sand being small fragments of flint, crystal, quartz, etc., is much harder than any body we know of that can be formed of lime only, which in paste is to be considered as a cement to the harder material, and therefore composes a harder body; for the same reason that if we had nothing naturally but lime as a cement, and should build a wall with flints, crystals, or rough stones cemented therewith, this wall would be harder than if built with lime alone."

**Vicat on the Use of Sand.**—Vicat, whose experiments on cement were, as we have seen, more careful and elaborate than those of most of his predecessors, cannot be trusted when he deals with the question of sand addition, for he could not in this case shake off the trammels of routine, and he accordingly regarded sand as a necessary part of mortar. He, however, lays down rules for the proportions of sand to be employed with fat and with hydraulic limes, which show a sound appreciation of the subject, and he points out that the quantity of sand must vary in accordance with whether the mortar is to be used in exposed or in protected situations. He asserts that the " intervention of pure sand does not tend as was before believed to augment the cohesion of which every kind of lime indifferently is susceptible, but it is injurious to rich limes, very serviceable to the hydraulic and eminently hydraulic limes, and is neither beneficial nor injurious to the intermediate kinds."

**Pasley's Rules for Use of Sand.**—Pasley, whose protracted investigations into the nature of cement mixtures and the influence of sand are so well known, did not fully recognise the facts of the case, for he seems to have thought that the strength of mortar was in some way or other related to its plasticity or pleasantness in working. He tells us that he found that Halling lime would not stand so large an addition of sand as the common chalk lime, and he proceeds to state, " every one will acknowledge that the proportion of sand which will make good mortar with chalk lime would entirely ruin cement, which is scarcely capable of bearing one-third of that quantity." Of course he had in view the Roman cement of those days which will take but little sand; but he spoke from the workman's point of view, and regarded a mortar as ruined when it was " too short for use." We now know that Portland cement will make a strong mortar with six volumes of sand, though few workmen care to use it when mixed in these proportions.

**Totten's Theory as to Sand Addition.**—We do not find any writer on

this question who is entirely to be trusted until we come to the experiments of General Totten, who employed a pure fat lime, and who clearly shows that each increase in the proportion of sand involves a falling off in the strength of the mortar; the lime alone furnishing the strongest mortar. His experiments are set forth in the following table, which we have extracted from the valuable essay of General Scott, published in vol. xi. of the Professional Papers of the Corps of Royal Engineers :—

| NATURE OF LIME. | COMPOSITION OF MORTAR. THE LIME MEASURED IN PASTE. | | | | | | |
| | 0 Sand. 1 Lime. | ½ Sand. 1 Lime. | ½ Sand. 1 Lime. | 1 Sand. 1 Lime. | 2 Sand. 1 Lime. | 3 Sand. 1 Lime. | 4 Sand. 1 Lime. |
| Smithfield fat lime, . | 262·5 | 245·6 | 222·5 | 214·7 | 170·3 | 154 6 | 135·1 |

The lime used in these tests was carefully ground in a mill and the mortars were moulded into prisms 6 inches long by 2 inches square in section. They were then subjected to a pressure of 600 lbs. for a few minutes, and after 50 days were broken by a force acting midway between the points of support, which were 4 inches apart. Three trials were made of each sample, and the highest breaking weight is in each case recorded. In all the experiments made by Totten he found that the strength of the mortar diminished as the quantity of sand was increased.

**Importance of the Size of the Sand Grains.**—The size of the sand grains and the proportion of solids to voids in any given sample of sand is no doubt a subject of much importance in making mortar. It is a matter of common knowledge that if a measure of known size be filled with dry sand, and if water is then poured upon it, the sand will settle down as the water is steadily added, and owing to a re-arrangement of the sand grains the mass will ultimately occupy a greatly reduced volume to that which it does in the dry state. Under certain conditions this shrinkage may amount to 25 per cent. of the volume. In the course of some experiments at Bermuda by Colonel Nelson, R.E., it was found that 1 part of lime powder when added to 3 parts of sand scarcely sufficed to fill the voids. In the form of paste it took 1 part of lime paste to fill the voids in 6 parts of sand.

The general experience is that coarse-grained angular sand produces a tougher and stronger mortar than a very fine-grained sand, though the latter works more sweetly under the trowel. This is probably due to the larger air spaces caused by the cavities or voids of relatively larger area. The average voids in sand have been found by careful measurement to amount to about 33 per cent. of the total volume occupied by it. No mortar can be regarded as wholly satisfactory in composition in which the voids in the sand are not filled up by the cementing material, because otherwise

certain of the grains might be in contact and have nothing between them, to hold them together.

**Scott on Proportion of Sand to be Used.**—General Scott, as the result of the careful consideration of numerous specifications, comes to the conclusion that if we are using the feebly hydraulic gray chalk lime, such as is generally employed in the London district, we may safely add 1½ parts or even 2 parts of sand to 1 part of slaked lime by volume. With a more hydraulic lime, such as that obtained from the lias formation, he would use 2 parts of sand to 1 part of slaked lime ; and with the pure chalk lime or the fat lime resulting from the calcination of a pure limestone, since the mortar so obtained is at all times very inferior, he states " if we are compelled to use such miserable stuff we shall not be losing much in resistance if we increase the quantity to 3 parts of sand to a part of lime."

**The Preparation of the Mortar.**—All the earlier writers on mortar laid great stress upon the thorough incorporation of the lime and sand, and it would seem by the price-books of the last century that in this country it took quite a day for a labourer to beat together the ingredients necessary to make 1 cubic yard of mortar. At the present time in all important works the mortar is mill-made, and in this way, no doubt, a far better mixture of the sand and lime is obtained than by the old-fashioned system of beating or larrying.

**Experiments on the Strength of Mortar.**—Many writers have experimented on the strength of the various descriptions of mortar, and it is not our intention to go into this question more in detail in the present chapter, as we shall have to revert to this branch of the subject in our chapter on cement testing.*

**Concrete.**—We have still to deal with the question of concrete, a term of recent origin, which has been considered by some authorities to be derived from the Latin word *concresco*. This may be taken to mean to grow together, or to consolidate. By " concrete," or the French word " *béton*," is meant a conglomeration of small stones embedded in a matrix of cement or mortar. There are natural examples of concrete in the " pudding stones," where gravel pebbles are united together by oxide of iron, or some similar binding agent, into a hard mass. Building with factitious stone was in use in very ancient times, and some writers have asserted that certain of the Pyramids of Egypt were constructed with artificial blocks of small stones and lime. Many of the earliest buildings in this country, dating back to the time of the Roman occupation, were evidently constructed of a species of coarse rubble-work, wherein fragments of stone and flint are embedded in lime mortar.

**Artificial Stone.**—As the knowledge of the properties of cements became

* In Chapter XX., p. 318, will be found some experiments by Mr. Kirkaldy on various descriptions of mortar.

extended, it soon occurred to ingenious minds that these materials might be employed in the formation of artificial stone, and this idea was first worked out upon a practical scale in France. Towards the close of the eighteenth century several inventors made known their processes for moulding a mixture of cement, sand, and gravel. The first experiments in this direction appear to have been due to a Toulouse architect, M. Lebrun. He used a specially prepared cement, which he made in a lime kiln ; this cement, to which he gave the name of " hydro," was composed of a mixture of lime, clay, and powdered coke or charcoal. The calcined material was ground and mixed with varying proportions of sand into a very stiff paste, with a minimum of water. This paste was at once introduced into the moulds and well rammed with a beetle. The artificial blocks made in this way were sometimes of a considerable size, and arches, with a span of upwards of 30 feet, were constructed under Lebrun's system.

**Ranger's Concrete.**—In this country the concrete constructions of Mr. Ranger, about the year 1832, for which he obtained patents in December, 1832, No. 6,341, and again in 1834, No. 6,729, attracted considerable attention. The wharf wall of Woolwich Dock Yard was erected by this process and its subsequent failure, due rather to insecure foundations than to a defect in the material, for a time brought concrete work into discredit.[*]

Vicat, in his work on mortars, describes a rude system practised in Piedmont for the production of artificial blocks of stone. Pits or trenches are excavated in a stiff clay soil to a depth of about 4 feet, and the sides are carefully trimmed to the requisite dimensions, and thus constitute a species of mould. A mixture of hydraulic lime and sand is then introduced, and large pebbles are inserted by hand in such a way as to cause the compound to be driven into all parts of the mould, the top is levelled off with a trowel, and then the whole mass is carefully covered over with about 2 feet of soil, and left for two or three years to become indurated. The lime used for this purpose is obtained at Casal, and is one rich in magnesia. The blocks formed in this way in a damp soil obtain a surprising degree of hardness, and may be dropped one on to the other from a height of 20 feet without injury.

**Concrete in France and England.**—In consequence of the inventions of M. Coignet in France, and of Mr. F. Ransome in this country, increased attention has in course of time been paid to the production of monolithic structures formed of gravel or ballast, aggregated together into masses by means of lime or cement. Concrete is really a mortar matrix, serving to bind together a suitable proportion of pebbles, flints, or broken stones. The amount of lime or cement to be used in making concrete must thus be to a certain extent determined by the nature of the material to be employed as aggregates. It ought theoretically to consist of a perfectly made mortar,

* See Pasley's *Limes, Cements, etc.,* p. 21, and Appendix, p. 301.

sufficient in quantity to fill the voids of the larger materials, for which it is to be used as the incorporating medium. The proportion of lime or cement may vary from one-seventh to one-twelfth of the aggregates, but no concrete can be really sound and good where the materials—the sand and gravel—are not properly adjusted. We mean by this that the lime or cement should be sufficient amply to fill the interstices of the sand, and the lime and sand mortar should properly fill the voids in the larger masses of stone. It has been found by careful measurement that while the voids in pebble-gravel will average about 34 per cent. of the volume it occupies when dry, the voids in broken stone may average from 40 up to 50 per cent. of the volume. Taking a mortar composed of 1 part of cement to 3 parts of sand, we might safely add, for the purpose of concrete-making, 3 parts of gravel to 1 of mortar, or 2 parts of broken stone. In some specifications, however, these limits have been dangerously exceeded, and there is sometimes a failure to apportion properly the sand and the larger aggregates. When concrete is merely used as a material for foundations in trenches this is not a matter of very great importance, but where the concrete is to be used moulded into blocks, or in order to form monolithic structures, it is very necessary to study these matters with care.

**Experiments of Mr. A. F. Bruce on Concrete.**—The observations of Mr. A. F. Bruce, who has carried out numerous experiments respecting the strength of Portland cement concrete, and whose investigations are published in vol. cxii. of the *Min. of Proceedings of the Inst. of Civil Engineers,* will show the importance of attending to these details. By careful manipulation of the ingredients and accurate adjustment of the proportions some excellent specimens of concrete known as "*bétons agglomerés*" are produced in France, and have been employed for very numerous purposes, for which stone or terra cotta is used in this country.

**Cement and Concrete Mixing by Machinery.**—Machinery has in recent years been introduced into all large works for the preparation both of mortar and concrete, to supersede the former slow and cumbrous method of hand-mixing. In the case of mortar-making many advantages are no doubt obtained by the use of edge-runner mills of sufficient size, especially where lime has to be incorporated with burnt ballast. In the case of cement mortars the employment of the ordinary mill seems to have a tendency to decrease the tensile strength of the mixture, and to retard somewhat the initial set of the cement, but if, for cement mortars, the rollers are taken out of a revolving-pan mill and replaced by a fixed arm with teeth, a very effective mode of mixing is secured, which greatly surpasses hand-gauging. For the preparation of concrete, numerous mechanical devices are available, all of which are immeasurably superior to hand labour, for in all of them a very intimate admixture between the cementing material and the gravel or ballast is secured, and great uniformity in the adjustment of the proportions is

attained.   In order to produce the best results, a careful study of the voids in the sand, as also in the substances to be concreted together, is, as already stated, indispensable.

**Armoured or Reinforced Concrete.**—The employment of concrete in construction is now making vast strides owing to the enormous gain in strength which is attained by the judicious use of an iron or steel core, or in the case of slabs or thin blocks, by the employment of wire netting or perforated iron plate, the so-called "extended metal." The weight of iron, which was formerly introduced in the shape of rolled joists, for instance, in flooring, has been proved to be quite unnecessary, and it suffices to employ twisted rods of small section, embedded in the centre of the concrete, to impart a degree of strength which is greatly in excess of that which would pertain to the sum of the strengths of the concrete and of the rods used separately. Experiments tend to prove that in armoured concrete the iron core acts in tension, while the concrete clinging round it is in compression.

# CHAPTER XXII.

## PORTLAND CEMENT CONCRETE IN SEA WATER.

LONG before the use of Portland cement, as an ingredient for concrete, became general, it had been the practice to employ hydraulic limes and quick-setting cements of the nature of Parker's and Roman cement for the preparation of concrete to be immersed in sea water. Even moderately hydraulic limes, when employed in conjunction with pozzolana or trass, have been found to give good results when introduced into works exposed to the action of the sea, but when the excellence of the concrete, prepared with Portland cement, became widely known, engineers quickly took advantage of the new material, and Portland cement concrete was specified without hesitation for marine constructions of all kinds.

The system of testing introduced by Mr. John Grant contributed, no doubt, very largely to the confidence felt in the quality of the cement itself, and the ready means provided for ensuring that the cement supplied was of the required strength, together with the relatively small cost of the tests advocated by him, speedily brought this material into widespread use for engineering purposes. We have seen that the cost of testing the cement, furnished over a considerable period to the Metropolitan Board of Works, was only about five farthings per ton of cement. No wonder than an ever-increasing number of works were carried out where concrete, deposited in masses, or somewhat later in monoliths of large size, was used freely, and it was considered, down to the middle of the eighties of the last century, that in Portland cement concrete, the engineer possessed a material for employment in sea water, which was both safe and durable.

A series of papers contributed to the Institution of Civil Engineers in November, 1886, described a number of important works in which concrete had been employed, both above and below water, with complete success. These works comprised piers, groynes, breakwater harbours and docks, both in this country and abroad, and while in some cases the concrete was simply dropped into the sea in the plastic form, steps being taken to avoid direct contact with the waves, by the use of skips or by means of boxes, bags, or frames in the nature of shuttering; in others ready-made concrete blocks of large size were prepared on land and allowed several months in order to become indurated, before they were lowered into their places in the sea. It is not necessary to describe more minutely the various works

or the methods actually employed in their execution, but that date is valuable as indicating the extent to which engineers had already employed the comparatively new material, and the confidence it had almost universally inspired. It was during the discussion on this group of papers that public attention was first called to certain failures in concrete structures, which were even then giving rise to considerable anxiety, and it was Mr. Harrison Hayter who voiced these strictures. He based his remarks, not only upon matters which had come under his own personal observation, but largely on the experience of a French engineer, M. Lechartier, who had contributed a paper to the *Comptes Rendus* of the French Académie des Sciences on this subject. He, like Mr. Hayter, had detected the presence of magnesia in large quantities in the concrete which had become softened in sea-water, and it was owing to the hydration of this magnesia that he believed that the disintegration of the Portland cement concrete was due. Complaint was made that English engineers did not, as a rule, cause cement to be analysed before use, and Mr. Hayter was also of the opinion that, in aiming at a material capable of yielding the high breaking weight test demanded at that time, cement manufacturers were using too much chalk in the compound. It was furthermore suggested that some restriction ought to be placed on the percentage of magnesia present in Portland cement, the contention being that "no Portland cement containing more than 1 per cent. of magnesia should be used." Mr. W. Smith, in describing failures of the work under his charge at Aberdeen Harbour, alluded to certain cases of softening of the cement, but he did not then refer to any deleterious action of the magnesia in the sea water.

It was, however, in consequence of the failures at Aberdeen that attention was subsequently directed to the influence of magnesia, present in the sea water, on Portland cement concrete, while for some time expert opinion on this subject was much exercised, and numerous theories were put forward to account for the destruction and decay of the concrete. Among the various experiments carried out to determine the precise behaviour of the magnesia none could have greater weight than those of the eminent German chemist, Dr. Michaëlis, who devoted much time to the study of this question, and who published many papers with respect to his investigations. Mr. Carey, whose opinions, also, carry great weight, made many special tests to determine the influence of the magnesia, and he sums up the result of certain deductions as follows :—" The quantity of magnesia in sea water, present as chloride and sulphate, amounts to 0·06 per cent. of weight. In a porous mass of concrete, a precipitation of the salts of magnesia takes place, some of the lime of the cement being at the same time dissolved. On the one side, it is held that these salts of magnesia, filling the pores and interstices of the cement, subsequently undergo a change of volume, producing disintegration. On the other hand, it is asserted that these precipitates are

absolutely inert, and do not in any way affect the strength of the concrete."

Dr. Michaëlis, while he regarded magnesia as a species of adulterant, when it replaced the lime of the cement, asserted that it had no useful action as a cementing material, and could not lead to any changes of volume greater than those which occur in normal cement, with up to 3 per cent., or even with much larger quantities of the magnesia.

An excellent summary of the facts relating to the concrete work at Aberdeen, which, as we have seen, was the starting point of the " magnesia controversy," is contained in a paper contributed to the *Proceedings of the Institution of Civil Engineers*, in November, 1891, by Mr. Wm. Smith. He refers to the investigations of Mr. P. J. Messent and Mr. Pattinson, who had been called in to advise, and gives the results of many tests and experiments specially undertaken to ascertain how far the deterioration of the concrete was due to chemical action. Both of the above gentlemen came to the same conclusion, which is summed up by Mr. Messent, as follows :—

" The presence of too much magnesia in the cement is the cause of the deterioration ; and that as the same proportion or quantity was not found in the neat cement used, the additional quantity found in the spoiled con-' crete must have been supplied by the sea water in contact with the cement portion of the concrete, which sea water, while precipitating the magnesia that it contains, takes away, in an altered form, a portion of the lime from the cement."

Experiments carried out by Mr. Smith proved that much of the concrete used in these works contained an undue proportion of aggregates, whereby it was undoubtedly rendered very porous, and the tidal action caused the sea water to pass backwards and forwards through the mass. The final result was that the calcium hydrates and possibly some of the silicates in the cement were decomposed. According to Professor Brazier, who made analyses of the injured concrete, the chemical reactions were as follows :—

$$MgCl_2 + CaH_2O = MgH_2O + CaCl_2$$
$$MgSO_4 + CaH_2O = CaSO_4 + MgH_2O$$
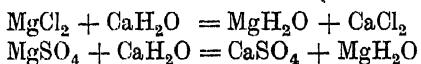
The sulphate of lime becoming crystallised with water led probably to the increase noted in the volume ($CaSO_4 + 2H_2O = CaSO_4 2H_2O$) as the crystallised sulphate in a substance of considerable bulk as compared with the lime base. It would seem from the actual results at Aberdeen, where the entrance walls expanded as much as $2\frac{3}{4}$ inches in height, and the surface of the blocks became cracked and bulged, that the chemical action was sufficiently intense to overcome the adhesive power of the cement, and that the entire mass of the concrete underwent gradual disruption. It was found, moreover, that voids in the interstitial spaces were filled by a white, creamy mass, composed mainly of carbonate and hydrate of magnesia.

As the outcome of this enquiry, Mr. Smith asserts that "the only certain and permanent method of building large masses of concrete or masonry for immersion in sea water under variable pressure is to make the entire mass impermeable," and he states that the weakest proportion of cement to ballast which can be considered permanently safe under the pressure of sea water is 1 to 4, or, say, 1 part of cement, 1½ of sand, and 2½ of stones.

In the course of the discussion on this and several other papers, read before the Civil Engineers at the same time, much valuable information on this question was elicited, and the general opinion was that the Aberdeen failure was caused by the use of porous and unsound concrete, containing an excess of aggregates. Mr. Carey said that "concrete as a material for structures in the sea was on its trial, a matter of vast importance to harbour engineers ; and it would be lamentable should doubt be raised as to the permanence of Portland cement for harbour works." He maintained that the question would have to be fought out on chemical evidence, and showed that in " scores of foreshore and sea works in cement concrete, scattered all over the world," there had been no traces of the " mysterious magnesian malady."

Both engineers and manufacturers were well represented on that occasion, and the results of many tests of the effects of magnesia, both in sea water and in solutions of various kinds, as also when it formed a component of Portland cement, were described. Some attempts made to blame the quality of the cement employed, as being overlimed, and to throw doubts upon the nature of the concrete, in that a certain amount of remixing of partly set material was permitted, were noticed by Mr. Messent, but he stated that the failures at Aberdeen were neither due to the use of cement of defective quality, nor to the practice of regauging and breaking up partially set concrete, which had been resorted to on this part of the works.

Dr. Michaëlis contributed to the same volume, in which these papers were printed, a valuable essay, entitled " The Behaviour of Portland Cement in Sea Water," wherein he lays great stress upon the importance of the production of a completely impermeable mortar, but he maintains that " many of the Portland cements in use at present are very unsuitable for marine work on account of their high proportion of alumina and ferric oxide, and their proportionately low percentage of silica." He states that the two compounds of lime, the aluminate and ferrate, are easily acted upon and softened by water, and that they tend to form double salts with sulphate of lime, the one containing alumina crystallising with considerable addition of water and increase in volume. He considers that the action of sulphuric acid in hardened cement gives rise to the formation of sulphates which may jeopardise the strength already attained and consequently break up the mass in the case of concretes. He asserts, moreover, that " the salts contained in sea water are the most dangerous enemies of hydraulic cements ;

the lime is either dissolved and carried off by the salts, and the mortar thus loosened; or the sulphuric acid forms with it crystalline compounds, such as basic sulphate of lime, alumino-sulphate, and ferro-sulphate of lime, which are segregated forcibly in the mortar, together with a large quantity of water of crystallisation, and a consequent increase in volume results." He regards the hydrate of magnesia always found in decomposed cement as " only the visible but completely innocuous sign of these processes."

It follows from the chemical analyses and many of the tests that for use in sea water most samples of Portland cement would be greatly improved by the addition of a small percentage of trass, pozzolana, or any substance rich in silicic acid, which would tend to combine with any superfluous lime and to form more stable compounds with the alumina and oxide of iron.

The troubles at Aberdeen were not the only ones with which engineers making use of concrete were called upon to deal, for very similar cases occurred at Maryport, and in a graving dock at Belfast. In the former place a wall 35 feet high lifted about 2½ inches, and at Belfast serious defects appeared in the concrete used in the construction of a dock. It would seem from a paper read before the Institution in November, 1892, that the Alexandra Graving Dock at Belfast was opened in 1889, and soon after the completion of the work cracks appeared in the concrete, which gradually opened out and allowed of the penetration of water charged with saline matters in solution. The floor also, which consisted of a bed of concrete 10 feet thick, showed " symptoms of disruption," and the cracks in the dock walls became wider. As the result of expert examination in June, 1890, made at the request of the Belfast Harbour Commissioners, it was reported that the cause of the decay of the concrete was the infiltration of sea water charged with salts of magnesia, which found its way from the adjacent tidal river and penetrated through the sandy backing into the lower part of the concrete surrounding the dock. The magnesia abstracted the lime from the Portland cement, which was conveyed away in an altered form, and the consequent chemical action caused the disintegration of the concrete. The remedy proposed was the removal of the decomposed concrete, and the substitution for it of a concrete, rich in cement, which should be as impervious as possible, and by this means put an end to the influx of sea water. It was pointed out in the course of the discussion on this paper " that it was only where the concrete walls were subjected to the unbalanced pressure of the tidal water that the destructive influences appeared to take effect."

In a later paper by Dr. Michaëlis, published in 1897, further results are given of the investigations conducted by him into the behaviour of cement in sea water. He maintained that in all samples of Portland cement there are considerable quantities of uncombined lime in the state of hydrate; thus, he says that a cement with 61·04 per cent. of lime would leave 13·79 per cent. of lime unsaturated, while one containing originally 68·379 per cent. of

lime (a cement quite too overlimed for ordinary practice) would leave a residue of 29·1 per cent. of lime unsaturated. In a sample of cement of average composition, with 1 part of silicate to 2 parts of lime, 25 per cent. of lime or 33 per cent. of calcic hydrate would be segregated. It is pointed out that no body, which contains a substance of such strong chemical affinity as free lime, can be regarded as stable. The free lime will undoubtedly continue to react, until it forms a saturated compound.

In the atmosphere, the lime is in time converted into carbonate, but this is a gradual process. In sea water it is chiefly the sulphates which act upon the lime, and further reactions occur between the alumina and ferric oxide, which may give rise to enormous increase in volume and disruption of the set cement. By exposing test-briquettes to the action of water from which carbonic acid was excluded Dr. Michaëlis was able to show that the strength was much below that of samples in which the formation of carbonate was possible. The magnesia which is deposited during the action of sea water upon hydraulic mortar is a preservative agent, which tends to close the pores of the mass, and thus serves to prevent the decomposition of the cement. It would be more correct, he said, to speak of the injurious action of the sulphates than to blame the magnesia which is wholly innocuous, although the magnesium sulphate is the special salt in sea water which causes the mischief.

All the above dangers may be avoided, as previously stated, by offering to the lime which remains, or is set free during the process of induration, hydraulic silica or alumina, with which it can form more stable compounds. Porous briquettes of cement mortar exposed to magnesia solutions rapidly show signs of disintegration, but when, instead of Portland cement alone, a mixture is made of equal parts of cement and trass, the attack in sea water is wholly arrested.

Dr. Michaëlis, after giving the results of many tests, sums up the matter as follows :—" The addition of trass or an efficient pozzolana to hydraulic cements containing an excess of lime, such as Portland cement, increases the strength of the mortar twice or three times, and renders them stable in sea water," and he says, " this is not surprising, because the best pozzolanas contain at least as much active hydraulic material as the best Portland cement."

After long controversy, it seems fairly certain that it is only porous and imperfectly mixed cement concrete which suffers from the injurious attacks of the salts in sea water, and that dense and sound concrete with proper proportions of aggregates may be regarded as entirely reliable.

# CHAPTER XXIII.

## THE GYPSUM CEMENTS.

CONTENTS.—Plaster of Paris as a Cement—Le Chatelier's Experiments—Preparation of Plaster—Plaster Kilns—Dumesnil's Improved Kiln—Coke-Ovens and Plaster Kilns—Use of Superheated Steam—Grinding of Plaster for Use—Gauging of Plaster—Researches by Landrin and Le Chatelier—Use of Alum—Keene's Cement—Martin's Cement—Staff.

**Plaster of Paris as a Cement.**—A whole series of cements, which have as their sole or chief ingredient sulphate of lime or plaster of Paris, depend for their set or induration upon entirely different properties to those which influence this reaction in the case of cements prepared from carbonate of lime. Calcium sulphate is found in a natural state in a great variety of forms, and is a substance of very common occurrence. As gypsum, the hydrated sulphate, the state in which it is perhaps most widely distributed, it contains in each 100 parts 32·60 of lime, 46·50 of sulphuric acid, and 20·90 parts of water, the chemical formula being $CaOSO_3 + 2H_2O$. There are numerous varieties of gypsum, some of them being transparent and crystalline as in selenite, some amorphous, and some fine grained and compact as in alabaster and plaster stone.

Calcic sulphate also occurs more rarely in the anhydrous state, devoid of water, when it is known as anhydrite, and it then consists of a crystalline mass with a regular cleavage into rectangular prisms. This mineral has not, so far as we know, been employed for industrial purposes.

**Properties of Calcic Sulphate.**—Sulphate of lime has a specific gravity of 2·31. It is slightly soluble in water (much more so than the carbonate). At a temperature of 60° F., 1 part of sulphate of lime will dissolve in about 490 parts of water. As the temperature rises the solubility increases until the water reaches 100·4° F., when the solubility again decreases. At the boiling point 1 part of sulphate will be contained in 571 parts of water, but by long-continued exposure to warm water the proportions may be varied somewhat considerably, and sulphate freshly precipitated is more soluble than gypsum. The raw gypsum or plaster stone is less soluble, moreover, than that which has been calcined. The industrial value of the sulphate of lime consists in the fact that the 2 equivalents of water with which we have seen that it is combined may be expelled at a temperature of about 392° F. A large part of this water may be driven off at a much lower temperature, and where the material is reduced to powder and kept well

stirred about three-fourths of the water may be expelled at a little below the boiling point of water, or about 205° F.

**M. Le Chatelier's Experiments.**—M. Le Chatelier, a French savant, who has carried out numerous interesting experiments in the dehydration of the plaster stone, and whose observations were communicated to the Académie des Sciences in 1883, has remarked that there are two distinct periods of rest during the process of expelling the water. His mode of demonstrating this fact was as follows :—Some pulverised gypsum was introduced into a hard glass tube, immersed in a paraffin bath, and gradually heated, the temperature being read off at regular intervals of time, by means of a thermometer imbedded in the plaster. By constructing a curve, showing graphically the increase of temperature for regular periods of time, it was seen that the heat rose rapidly to 230° F., then more steadily from 230° to 248°, remained for some time nearly stationary between 248° and 266°, then rapidly increased between 266° and 284°. A second, but minor, halt in the process took place between 320° and 338°. These two interruptions indicate the absorption of heat which accompanies the elimination of water, and point to the existence of two different hydrates, whose decomposition takes place at differing ranges of temperature.

The first of these compounds is represented by the formula commonly used for gypsum—viz., a hydrate in which 1 part of the calcic sulphate is combined with 2 parts of water $CaSO_4 + 2H_2O$. This substance parts with three-fourths of its water to form the second hydrate, in which 2 parts of the sulphate are united to 1 equivalent of water, which compound would be represented by the formula $2(CaSO_4) + H_2O$.

**Commercial Plaster is a Hydrate.**—The existence of this hydrate was clearly shown by M. Le Chatelier, for on heating for some time 10 grammes of powdered gypsum at a temperature of 311° F., which is intermediate between that needed for the decomposition of the two forms of hydrate, he ascertained that the loss of weight was uniformly 1·56 grammes, which corresponds very precisely with 1½ equivalents of water, and from this it is clear that the compound thus obtained contains only half an equivalent of water, combined with the sulphate, or about 6·2 per cent. Ordinary commercial plaster of Paris as prepared for use contains, as a rule, about 7 per cent. of water, and hence it consists almost exclusively of this particular hydrate.

**Plaster Burnt at High Temperatures.**—On submitting the plaster to a temperature of 338° F. and upwards no change is apparent, so long as the heat does not exceed 390° to 430°, but beyond this point the material begins to lose certain of its essential properties. It ceases to absorb water with avidity, and sets only after a long interval of time. If the heat reaches 650° it cannot be gauged in the ordinary way, and comports itself exactly like anhydrite. In this state it is termed " dead-burned."

**Overburnt Plaster Combines very slowly with Water.**—It has sometimes been asserted that plaster thus treated can no longer combine with water, but this is an error, as the hydration can still take place if the substance be reduced to a very fine powder; the process is, however, greatly retarded. On continuing the calcination of the plaster to the temperature of bright redness, the substance melts into a vitreous paste, which forms a crystalline mass on cooling, having all the attributes of anhydrite, which is no doubt a native gypsum, acted upon by volcanic or similar agencies. It is impossible to decompose this substance by heat, but if strongly heated in contact with charcoal, or in the presence of decomposed organic matters, it loses part of its oxygen and is converted into calcium sulphide, which substance is in turn acted upon by carbonic acid and water, giving rise to the evolution of sulphuretted hydrogen gas. It is in this way that we are able to explain the presence of sulphuretted hydrogen gas in certain mineral waters, originally containing sulphate of lime in solution. When waters rich in dissolved sulphate of lime are used in boilers, or when sea water is employed, a deposit or scale is formed, which consists mainly of the hydrated sulphate with half an equivalent of water, or one in which water is present to the extent of some 6 or 7 per cent. The mean of several analyses of boiler-scale from a marine boiler show this substance to have the following percentage composition :—

| | |
|---|---|
| Carbonate of lime, | 0·3 |
| Peroxide of iron, | 2·0 |
| Water, | 5·8 |
| Sulphate of lime, | 91·9 |
| | 100·0 |

**Preparation of Plaster requires great Nicety.**—It will be evident from the foregoing observations that the preparation of plaster of Paris is a matter of considerable nicety, and that the degree of calcination requires attention and care, for while, on the one hand, too high a temperature produces a more or less inert substance ; the failure to expel the water of hydration renders the material useless for moulding and casting, which, at any rate in this country, forms one of its chief uses. In many parts of France coarse plaster takes the place of lime mortar, and impure sulphates, or those mixed with small quantities of slaked lime, appear to be well adapted for this purpose. Moreover, precautions must be taken in burning the plaster to avoid direct contact with the fire, as carelessness in this respect leads, as we have seen, to the formation of calcium sulphide, a very objectionable product.

**Preparation of Plaster formerly practised.**—The oldest and simplest plan of burning plaster-stone, and the one which is still most commonly employed abroad, is effected in a rude shed, enclosed on three sides by walls of brick or stone, and roofed in to protect the contents from the weather.

As will be seen by Fig. 101, the floor is sometimes hollow, and upon it the stone is built in a series of rough arches, x, x, x, disposed parallel to the main walls of the building, these arched flues are constructed of the largest lumps of stone, and immediately over them are placed the lumps next in size, the smaller pieces being next selected, and the size of the pieces of stone decreasing upwards as the heat from the fire diminishes, the top of all being covered in with dust and sweepings. Wood fires are then lighted in each flue, and these are regulated so as to produce a moderate heat, and they are kept going as steadily as possible in order to maintain an equable temperature throughout the entire mass of stone. The flames pass upwards through the interstices of the material and drive off the moisture and the
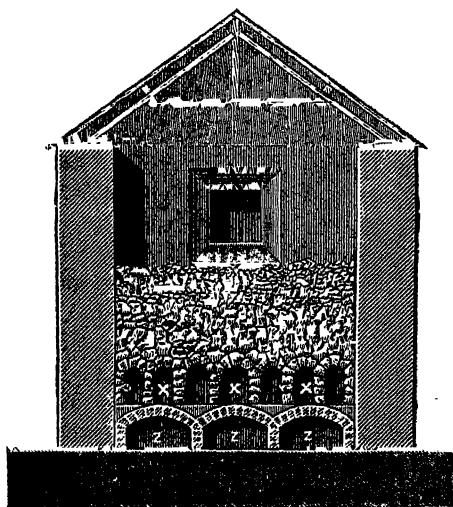


Fig. 101.—Covered Hovel for Burning Gypsum.

water of hydration, which escape in the form of dense vapours, and pass out through openings in the roof and in the upper part of the shed.

**Plaster Burnt with Coal.**—When coal is employed in the calcination, rude furnaces are formed in the arched spaces beneath the floor, as seen at z, z, z in our illustration, and the flames pass through special apertures contrived in the tops of the arches. The firing is continued until the arch stones at the base of the mass show visible redness, say for about twelve hours, after which the fires are drawn and the plaster is allowed to cool slowly. It will readily be seen that this plan is a very unscientific one, for while the top layers are often barely deprived of their combined water, the lumps forming the voussoirs of the arches are overburnt, and yield a

partially if not wholly inert plaster. In spite of every care also, it is impossible to prevent the formation of a certain percentage of calcium sulphide, which gives rise to the unpleasant smell of sulphuretted hydrogen always apparent when plaster made in this way is gauged with water, and the presence of this sulphide is very unfavourable to the setting of the compound.

**Preparation of Plaster in the Vicinity of Paris.**—A much better system of dehydration is that practised in the vicinity of Paris, for which a kiln is employed somewhat resembling in form those used for lime, but furnished with an arched cavity at the base, formed of fire-bricks and pierced with openings for the passage of the flame and heat. In a suitable kiln of this description the heat can be more evenly distributed, but it has the same
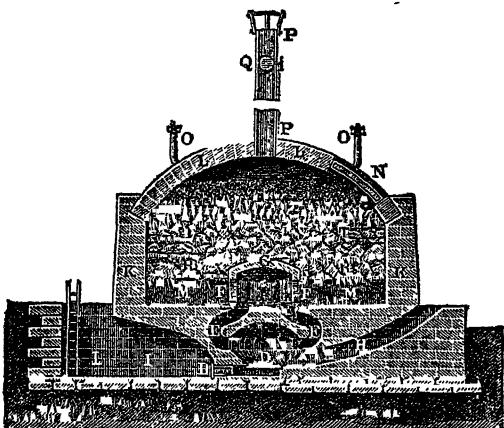


Fig. 102.—Transverse Section of the Dumesnil Kiln.  Fig. 103.—Plan of Plaster Kiln.
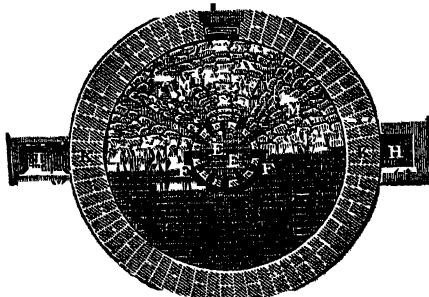
objection as the one we have previously noticed, in that the bottom layers receive much more heat than those at the top, and the product, even with the utmost care, is never uniform throughout.

**Plaster Kilns of Improved Construction.**—A kiln which is much better in principle, in that the heat is under more complete control, and can be imparted more evenly to the whole of the contents, is that invented by M. Dumesnil, shown in Figs. 102 and 103. This kiln is circular in plan and has a central furnace, D, above which is the fire chamber, G, formed of fire-brick and furnished with twelve-openings at F, F, F; the flame passes from the furnace into the chamber, G, by curved flues, seen in section at E, E. Each of the openings at F is connected with a radiating flue, M, constructed with lumps of plaster built into the form of an arch. Above these flues the stone is arranged in layers, R, S, T, the larger pieces of stone being placed near the bottom and the smaller fragments in the upper layers. The top of the

kiln is arched, and has one central and four smaller flues, all of which can be closed by means of dampers. In the arched roof, L, L, is an orifice, N, for filling the top of the kiln, while a door in one side serves for emptying and loading. The stoke-hole is shown at H, and the ashpit at I. In burning this kiln, which is 20 feet in diameter and 13 feet to the top of the arch, the contents are dehydrated by means of a moderate fire in about twelve hours, and then the fires are extinguished and an extra charge of 6 or 7 cubic
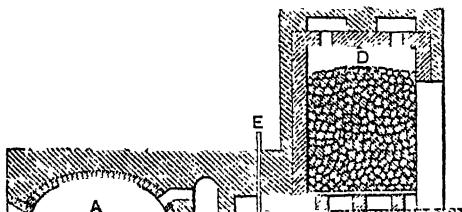


Fig. 104.—Section through Combined Coke Ovens and Kilns.
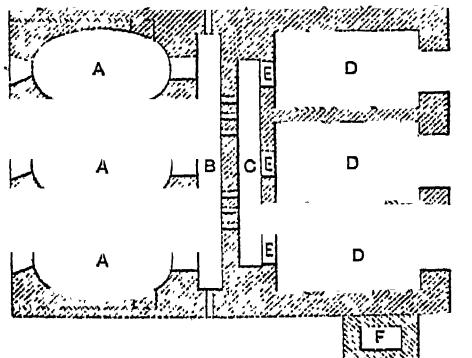


Fig. 105.—Plan showing Combined Coke Ovens and Plaster Kilns.

yards of stone is added above the top layers, after which all the openings are closed, and the heat of the former charge is sufficient to effect the dehydration of the topping. The contents of this kiln are found to be about 45 cubic yards. The kiln is economical to work in the matter of fuel-consumption, and the products are fairly uniform in quality, but the first cost of its erection is very considerable.

**Other Methods of Burning Plaster Stone.**—Various other plans for burning plaster stone have been from time to time introduced, some of them with a

fair measure of success. Thus the waste gases from coke ovens have been utilised to heat the stone, and the arrangement of the kilns and ovens for this purpose is shown by Figs. 104 and 105. Here A, A, A are coke ovens of an ordinary type which discharge their surplus heat into a collecting flue, B. This flue communicates with a subsidiary flue, C, leading to the plaster kilns, D, D, D. · It is possible, by means of dampers at E, E, E, to turn the heat into any one or more of a series of kilns. The floors of the kilns are perforated, and the flames pass up into the charge of plaster stone, which is piled up to a considerable height. The steam and waste heat finally escape by means of a collecting flue running along the tops of the kilns into the chimney, F.

**Use of Superheated Steam.**—Superheated steam and gas have also been employed successfully. When steam is used it is raised to a temperature of about 390° F. and blown alternately into each of two chambers filled with raw stone. The high temperature of the steam rapidly abstracts the water of hydration and leaves the plaster in a condition ready for grinding. Some experiments upon a small scale conducted by M. Violette led him to the conclusion that 3 cwts. of gypsum could be dehydrated in three hours by a current of superheated steam, amounting in weight to about 132 lbs.

Several processes have been brought forward for dealing with the plaster stone in continuous kilns, or " running kilns," resembling somewhat those used by lime burners, and a process of roasting in cylinders caused to rotate, or furnished with a creeper or spiral screw, so as to move the plaster continuously forward from one end to the other, has also been tried. Many of these plans have resulted in the production of plaster of good and uniform quality, and free from the impurities and imperfections arising from the crude and unskilled processes in common use.

**Best Plaster Prepared by First Grinding the Raw Stone.**—For plaster of the best description, capable of setting quickly, and ensuring hard and durable casts, moulders prefer to obtain the raw stone for themselves, and to grind the same to a fine powder. This powder they then prepare for use by a so-called process of " boiling." The plaster meal is spread in a layer, some 2 or 3 inches in depth, upon a hot plate or in a shallow metal dish over a fire ; in a short time, when the temperature approaches that of boiling water, a strange motion is communicated to the whole mass of the material, and the surface appears to rise up bodily as if suspended by the aqueous vapour given off by the lower layers. Little openings or craters are formed all over the surface, and the steam passes off freely, mingled with fine dust. From time to time the plaster is stirred, and care is taken to avoid an excess of heat. When no further evolution of moisture takes place, which can be tested by holding over the surface a cold plate of glass or metal, to condense the steam, the heat is withdrawn, and the plaster is ready for use. When

prepared in this way, the combination with the water used for gauging takes place with great rapidity, and sound and hard casts are produced.

**Plaster Baked in Special Ovens.**—Much of the plaster used in this country is baked in ovens, constructed on the principle of the baker's oven. In this case the stone is broken into lumps about the size of a small hen's egg, and is introduced into a well-heated oven, the temperature being but little greater than that used in baking bread. It may be tested by inserting the hand, which should be able to bear the heat for two or three seconds. The oven is then closed up, and specimens are from time to time withdrawn, to ascertain if the dehydration is complete ; the baking may last from twelve to twenty hours. The man in charge of the operation is able to judge, by the colour and appearance of the lump removed, if the water is expelled. Properly burnt stone exhibits on the white earthy fractured surface only a few bright specks here and there of crystalline particles, not completely deprived of the water of hydration. When the stone has been cooled it is ready for grinding.

**The Grinding of Plaster for Use.**—The grinding of plaster is a very simple matter, and almost any contrivance for this purpose will give good results. In some cases edge-runners or rollers are used, but the best meal is produced by mill-stones, such as are employed for grinding flour. Evenness and regularity of grain are most essential in the case of the best quality of plaster used for casting purposes. Such plaster has a soft, smooth feel to the touch, and sticks slightly to the fingers. It has, in fact, rather a tendency to cake together when compressed, while plaster which has not been sufficiently dehydrated has a dry and slightly gritty feeling. Overburnt plaster shows little tendency to absorb water, and cracks when made up with water. The ground plaster should be kept as far as possible from contact with the air, and not merely be placed in sacks, as is too often the case. The powder has a strong tendency to absorb moisture, after which it becomes slow-setting, and yields a less solid casting. In France heaps of plaster are sometimes kept in good condition for a long period (even for a year) by slightly wetting the outside of the mass with a watering can. By this means a preservative crust is formed which suffices to protect the interior of the heap.

**The Gauging of Plaster.**—The gauging of plaster, as the mixing of the same with water is termed, always gives rise to an elevation of temperature, due to the hydration of the calcium sulphate, and this is a similar reaction to that which takes place when lime is slaked. We have seen that, in accordance with the temperature at which it has been burned, the gypsum is more or less fully deprived of its water of hydration, and that its recombination with water takes place with so much energy as to cause a considerable rise in the temperature of the mass. There is, at the same time, an increase in bulk, which may amount to as much as 1 per cent. in 24 hours after gauging. The volume of water employed has some influence upon the rapidity of the

set, and upon the ultimate hardness of the plaster, but even with a very considerable excess of water the plaster has still the power of setting, which we know is not the case with quicklime. It is an axiom in plaster mixing that the plaster should be gradually introduced into the water used for gauging, and not the reverse as is sometimes the practice. While the mixture is being made the whole mass must be kept well stirred, by which means the formation of lumps and air-bubbles is avoided. The commonly received opinion respecting the setting of plaster is that the process is not only one of hydration, but that simultaneously a crystallisation of the mass takes place. The particles of the powder are converted into a porous network of crystals, which enclose in their interstices a certain proportion of the water containing sulphate of lime in solution. This water is held mechanically, and speedily evaporates, causing the dissolved sulphate to crystallise out, and thus adds to the hardness of the already-formed mass.

**M. Landrin's Investigations into the Set of Plaster.**—M. Landrin, who has investigated the behaviour of plaster with water microscopically, confirms this opinion, and assigns three distinct phases to the operation of setting. First, the plaster assumes on the contact with water a crystalline structure ; second, the surrounding water dissolves a portion of the sulphate of lime ; and third, a part of the liquid evaporates, owing to the rise in temperature caused by this chemical action, a crystal is formed and determines the crystallisation of the entire mass, in consequence of a phenomenon analogous to that which is observable when a crystal of sodium sulphate, containing 10 molecules of water, is thrown into a saturated solution of that salt.

**M. Le Chatelier's Researches.**—It appears that in 1883 M. Le Chatelier, in a communication upon this subject to the Académie des Sciences, pointed out that a direct transformation, according to the theory hitherto accepted, of the solid anhydrous sulphate of lime into the solid crystalline hydrated sulphate, would constitute an exception to the general law of crystallisation, and, moreover, the mere fact of crystallisation would not necessarily entail the aggregation of the mass. Thus, for instance, calcium sulphate, precipitated by means of alcohol from a concentrated solution, presents a maximum amount of entanglement of the crystals, but the precipitate when dried shows no tendency to cohere together into a solid mass.

**New Theory as to the Process of Setting.**—In order, therefore, to account for the setting of plaster and of other analogous substances, M. Le Chatelier has been compelled to formulate a new theory, based upon the phenomena of supersaturation investigated by Marignac.

**Observations by M. Marignac.**—This observer has shown that the hydrated calcium sulphate with half an equivalent of water, which remains undecomposed at a temperature of about 310° F., dissolves freely when shaken up with water, but that after a short interval the solution becomes turbid.

This is due to the formation of a crystalline precipitate of the common hydrate with two equivalents of water, which has the formula of gypsum. The solution formed in the first case is five times as concentrated as that made from the less completely hydrated sulphate. It would appear from this that the most important agent in the accomplishment of the setting process is the relatively soluble hydrate—namely, that with a small percentage of water. This hydrate is at once dissolved, and then gives rise to the formation of the other hydrate, with the full equivalent of water. This latter compound decreases the solubility of the mixture, and the water becomes supersaturated with the $CaSO_42H_2O$ hydrate, which crystallises out. This process continues so long as there remains any of the soluble hydrate $[2(CaSO_4)H_2O]$ to fortify the solution.

The set of plaster is thus the result of two distinct series of operations, which take place simultaneously; first the particles of calcium sulphate in the act of hydration are dissolved in the water used to gauge them, and produce a supersaturated solution; the solution thus formed deposits crystals of the hydrated sulphate. These crystals gradually increase in size, and form a compact mass, in the same way as do all similar crystals deposited slowly from a saline solution, and this process is continued as long as any of the more anhydrous sulphate remains available to become dissolved and to keep the solution supersaturated.

**Connection between this Process and the Induration of Cements.**—This theory has, we believe, a somewhat important bearing on the set of calcium silicates, and the transference of the soluble lime to the crystalline silicates may take place in a somewhat similar way. It is on this account that we have reproduced, at some length, the valuable remarks of M. Duquesnay in the *Encyclopédie Chimique* treating of this subject.

**Substances used to Improve Plaster.**—It has long been known that a variety of substances are capable of imparting to the somewhat soft and friable composition of the set plaster a greatly increased hardness and consequent durability. Gay-Lussac has pointed out that the hardest crude gypsum yields, after calcination and reduction to a powder, the hardest casts. This same property, so far as mortar was concerned, was, as we have seen, erroneously ascribed to dense and hard limestones. We learn from Tissot that if burnt gypsum, after it has become set, be repeatedly steeped in water and allowed to dry between each soaking, it will greatly improve the crystallisation of the mass and will result in a much harder casting. If six parts of plaster are intimately mixed with one part of freshly-slaked lime and used for casting purposes, and the object when made is steeped in a concentrated solution of magnesium sulphate, it becomes so hard, when dry, that it can scarcely be scratched with the finger nail. Various silicates in solution, as " water-glass," may also be used to harden plaster of Paris.

**Alum used with Plaster.**—The most common method, however, of

hardening plaster depends upon the employment with it of alum, under a plan proposed, in the first instance, by Pauware, and improved upon subsequently by Greenwood. Alum may be used in two ways, either the finished casting may be steeped in a strong solution of alum, and then be slowly dried in a current of warm air—a process which needs at least a month in the bath—or the lumps of plaster when withdrawn from the kiln may be treated with a solution of alum, and then again raised to a red heat in a suitable kiln or oven. The heat in this second burning must be much greater than that needed for the dehydration of the gypsum. It is very necessary also that the heat during this second firing should be steady and uniform. The lumps when properly burnt have a dull milk-white or even a pale yellowish tint, but if the calcination is carried too far the lumps become as hard as stone, and are very difficult to reduce to powder. A composition of gypsum and alum, burnt at the requisite temperature, is readily ground, and when pulverised and gauged with water sets as rapidly as common plaster, but the resulting cement is not remarkably hard, unless the water employed consists of a solution of alum, containing from $\frac{1}{12}$ to $\frac{1}{15}$ by weight of alum. The casts obtained by this process continue to give off moisture or to " sweat " for a longer period than those made with ordinary plaster, but they acquire in time a degree of hardness comparable with that of alabaster or even marble, and they are capable of receiving a high polish. The surface has a creamy tint, and objects made in this alum plaster, being much less soluble, will bear exposure to the weather, and will even resist the prolonged action of boiling water. It has been observed that these castings are to some extent semi-transparent, and transmit a certain amount of light through the thinner portions.

**The Theory of the Action of Alum.**—Various reasons have been alleged for this action of alum on plaster. Payen supposed that the induration was owing to the formation of a double sulphate of lime and potash, the crystals of which were embedded in a precipitate of alumina, but this surmise has been controverted by the investigations of M. Landrin, who found by the analysis of numerous specimens of plaster treated with alum, both of French and English manufacture, that these substances were almost absolutely pure and free from alumina and potash. The results he obtained are seen in the accompanying table. Nos. 1 and 4 are French samples, and Nos. 2 and 3 are of English make.

| Alum Cement. | Sulphate of Lime. | Carbonate of Lime. | Silica. | Water. | Total. |
|---|---|---|---|---|---|
| 1, . . | 96·75 | 1·05 | 0·72 | 1·48 | 100 |
| 2, . . | 98·19 | 0·41 | ... | 1·40 | 100 |
| 3, . . | 98·02 | 0·37 | 0·42 | 1·19 | 100 |
| 4, . . | 98·05 | 0·36 | 0·51 | 1·08 | 100 |

**New Theory by M. Landrin.**—Seeing that these samples were all so free from water, it may be assumed that they were in each case burned at a high temperature, and the absence of potash and alumina led M. Landrin to propound an entirely different hypothesis. He came to the conclusion that the action of the alum was caused by its contents in sulphuric acid, rather than by the bases present therein, and that this acid led to the conversion of the carbonate of lime into a sulphate of lime. In order to ascertain the accuracy of this surmise, he made use, in the first place, of a number of soluble sulphates, such as the sulphates of soda, potash, and ammonia, and caused them to act upon common plaster. He took care to employ only the precise amount of each of these substances which would furnish the supply of sulphuric acid needed to act upon the carbonate of lime, and he obtained precisely the same results as with alum. Parallel experiments, with sulphuric acid alone, gave, as he anticipated, corresponding results, and he was thus enabled to indicate a new process for the preparation of alum-plasters. All that is needed to impart the same degree of hardness as that due to the use of alum is to steep the raw plaster stone for about a quarter of an hour in a 10 per cent. solution of sulphuric acid and then to fire it at a dull red heat. By this means he obtained an excellent plaster cement, which left nothing to be desired in point of hardness, and which was sufficiently slow-setting. Moreover, the effect of the dilute acid was to destroy all traces of organic matter (always found in the raw gypsum, and which tend to give it a greyish colour), and to bleach it most perfectly, so that the resulting cement was exceptionally white and pure.

**Importance of Expelling the Acid.**—It must be remembered, in connection with this process, that it is absolutely essential that all the uncombined acid should be expelled, as even slight traces of sulphuric acid would render the plaster more or less hygroscopic and liable to attract water. The burning should, on this account, be carried out at a temperature of from 1,080° to 1,260° Fahrenheit. As the effect of adding the alum is, as we have thus seen, merely to augment the amount of calcium sulphate present in the plaster, we can only attribute the slowness of the set to the influence of the high temperature at which it is burned, and there is thus a complete uniformity of action between the alum or sulphate plaster and that prepared in the ordinary way.

**Keene's Cement.**—Several other plaster cements have become widely known in this country, and they are for the most part prepared in a similar way to that we have described in the case of M. Landrin's process, only using a different solution. Keene's cement is made by steeping the calcined stone in a strong solution of borax and cream of tartar. The liquor is composed of 1 part of borax and 1 part of cream of tartar, dissolved in about 18 parts of water. In this solution the plaster in the lump, as withdrawn from the oven, is allowed to remain until it is thoroughly impregnated with

the salts. It is then taken out, dried, and reburned at a temperature of dull redness for about six or eight hours. When cool it is ground to a fine powder, and it is ready for use. It is found that borax alone gives equally good results, and the more concentrated the solution into which the plaster is introduced the slower is the ultimate set. Thus, if to 1 part of a saturated solution of borax we add 12 parts of water, and employ this liquid as the bath, the set will take place in about fifteen minutes; but if only 8 parts of water be used, the cement will take at least an hour to set; and if 4 volumes of water be used, the cement will only become set after the expiration of several hours. The manufacture of Keating's cement is similar in all respects to the process employed by Keene.

**Martin's Cement.**—In the preparation of Martin's cement the solution employed is one of carbonate of potash, the stages of the manufacture being similar to those already described. For Parian cement, the bath employed may contain borax, but we understand that it is also prepared by calcining an intimate mixture of powdered gypsum and dry borax, which mixture is subsequently ground to a fine powder, which constitutes the finished cement.

Respecting the chemistry involved in the production of these cements, Knapp remarks that their action is probably due to the fact that one equivalent of water contained in the gypsum is capable of being replaced by a saline compound, and that possibly these substances have the power of completely taking the place of a portion of the water, and thus giving rise to the greater degree of hardness attained by the compound. A solution of tartrate of potash and soda (seignette salt) causes plaster to set instantaneously. The indurated mass has the appearance of ordinary gypsum, but it possesses the property, when it is repulverised, of again becoming hard when moistened with a solution of a salt of potash. Knapp's theory, it may be remarked, does not agree with that of M. Landrin. Many of these reactions are very interesting, and merit further study, which might lead to important industrial results.

**Staff.**—It seems necessary, seeing the vast extent to which this material is now employed for the purposes of decoration, and even for the construction of buildings of a temporary character, to say something of staff, which is a species of fibrous plaster, or plaster of Paris toughened and bound together with tow. In England this substance is generally known as fibrous plaster, as this was the name given to it by its inventor, Desachy, a French modeller, who took out a patent for it in 1856. It seems doubtful whether this was really a new invention at that time, but it has come to be very widely used for ornamental purposes, and at the Paris Exhibition of 1878 many of the most imposing structures relied upon this material for their decorative treatment, and the fibrous plaster was still more largely employed in 1900. The ordinary staff is made of plaster and Manila fibre, and the mixture is

generally used upon a backing of coarse canvas, of very open texture, called " scrim." Any cheap fibre may be used, and for fireproof purposes the plaster may be incorporated with asbestos. For some purposes it is mixed with slag-wool or coke breeze. The moulds in most cases are made of gelatine on a plaster core. It is claimed that alum water applied to the mould at the time of casting hardens its surface, and causes the plaster to set more quickly ; this would be in accordance with what has been previously stated with respect to alum solutions.

# CHAPTER XXIV.

## CEMENT SPECIFICATIONS.

IN former editions, we have endeavoured to show, by selecting some of the chief specifications then in use by various public bodies, the great diversity of opinion prevalent respecting the requirements of cement users, and we consistently urged the need of some generally recognised rules for the uniform testing and delivery of Portland cement. We published in our second edition the specification employed by the Metropolitan Board of Works, which had the authority, no doubt, of the late Mr. Grant, as also the skeleton specification prepared by him in 1880. We printed many of the forms issued by large cement users, including the rules of the American Society, and we concluded with the hope that "unanimity may ere long be established." We pressed, also, as we have often done before, for the issue of " a standard form of specification."

The British Standard Specification issued under the auspices of an influential Committee of the Institution of Civil Engineers was first prepared in 1904, and has now been several times amended. We requested the Committee to permit us to publish a copy of this Specification in the present volume, but we are informed that it has been decided that, as this document is published officially, and that as the work of the Committee of Standards is partly supported by the sale of its publications* no further authorisation will be granted for the use of these documents by authors in treatises on cognate subjects. We have in several places made brief references to the " Standard Specification," and can only say that we are heartily in accord with the various clauses and with the rules laid down, which have already done great things to improve our English cement manufacture.

We print here a translation of the latest issue of the German Standard Specification in its most recent form as issued in 1909, omitting the final section dealing with the preparation of the test samples, and we give also the present " Cahier des Charges Français," prepared by the Ministry of Public Works, which has the authority of a Standard Specification.

* The Cement Specification is now published by the Committee at a shilling.

### German Standards for the Uniform Delivery and Testing of Portland Cement.*

1. **Explanatory Definition of Portland Cement.**—Portland cement is a hydraulic binding agent containing not less than 1·7 equivalents by weight of lime (CaO) to 1 equivalent of soluble silicic acid $(SiO_2)$ + alumina $(Al_2O_3)$ + oxide of iron $(Fe_2O_3)$ produced by the pulverisation of the ingredients to a finely divided state, intimate admixture of the same, calcination, at least to incipient fusion, and fine grinding. Not more than 3 per cent. of any other substance may be added to Portland cement for any special purpose.

The contents in magnesia must not exceed 5 per cent., and those of sulphuric anhydride not more than $2\frac{1}{2}$ per cent. of the weight of Portland cement heated to bright redness.

#### BASIS AND EXPLANATION.

Portland cement differs from all other hydraulic cementing agents by its high lime contents, which involves an intimate mixture of the raw materials in very exact proportions. These can only safely be secured (except in the case of a very small number of natural substances) by artificial means. by extremely fine grinding or by the formation of a slurry together with the most intimate admixture under chemical control.

In the interests of the consumer, it must be stipulated that similar products obtained from natural substances by simple calcination should be described as " Natural Cements."

By calcination to the clinkering point (incipient fusion), the product obtained has· very great density (volumetric weight), which is an essential property of Portland cement.

The presence of magnesia up to 5 per cent., which may occur when a dolomitic limestone is employed, has been proved to be harmless when, in estimating the lime contents, the magnesia has been included with the lime.

In order to render the Portland cement slow-setting, it is customary to add raw gypsum (aqueous calcic sulphate) to it during the process of grinding, but, apart from this, all Portland cements contain sulphuric acid compounds derived from the raw materials and the fuel.

Additions for specific purposes—namely, in order to regulate the setting time—are not to be forbidden, but they are limited to 3 per cent., in order to exclude the possibility of additions to increase the weight. The presence of sulphuric anhydride up to $2\frac{1}{2}$ per cent. in amount has been proved to be free from injurious effects.

2. **Packages and Weight.**—Portland cement is usually packed in sacks or casks. Each package, in addition to the gross weight and the words " Portland Cement," should bear the name of the manufacturer or the trade mark of the factory marked in plain figures.

* Translation by Gilbert R. Redgrave.

Leakages or other variations in the weight of individual packages may be allowed not exceeding 2 per cent.

### BASIS AND EXPLANATION.

In the case of packages made up both in sacks and casks, differences occur in the weights, it is, therefore, imperative that the gross weight should be given.

By the use of the words " Portland Cement " the customer is assured that the goods comply with the foregoing definition.

3. **Setting Process.**—The initial set of normal-setting Portland cement must not take place earlier than one hour after gauging. For special purposes, more rapidly setting Portland cement may be required, and this must be described as such.

### BASIS AND EXPLANATION.

The beginning of the period of initial set of normal-setting Portland cement was fixed at not less than one hour, because the beginning of the initial set is of importance. On the other hand, the determination of a specified setting time was not insisted upon, because in the use of Portland cement it is of minor importance whether the setting process ends in a shorter or longer period. Any regulations with respect to the duration of the setting time should, therefore, not be too strictly defined.

In order to ascertain the setting time of a Portland cement, 100 grammes of the pure slow-setting Portland cement must be stirred into a stiff paste with water for three minutes, but only for one minute in the case of a quick-setting cement, and formed into a pat $1\frac{1}{2}$ centimetres in thickness, but thinning out at the edges, on a glass plate. The consistency of the Portland cement paste required for the production of the pat should be such that, when placed on the surface of the plate with a spatula, it will only flow outwards to the edge after a series of taps upon the glass; for this purpose from 27 to 30 per cent. of water will generally suffice. The beginning of the stiffening process should be recorded.

In order to determine the beginning of the hardening process and to ascertain the setting time, recourse is had to the cylindrical normal needle of 1 square millimetre in cross-section and 300 grammes in weight, with a flat end cut off at right angles to the axis of the needle. A conical ring of ebonite is placed on a glass slab. This ring is 4 centimetres in height and 7 centimetres in mean clear diameter, and is filled with the Portland cement paste (about 300 grammes of the cement needed) of the above consistency. It is then placed beneath the needle. The period of time when the normal needle is no longer able to penetrate the paste entirely is to be regarded as the beginning of the setting time. The time which elapses until the norma

needle fails to make any noticeable impression upon the stiffened pat is taken as the setting time.

As the setting of cement is influenced by the warmth of the atmosphere and that of the water used for gauging, inasmuch as high temperatures tend to hasten the setting time and low temperatures cause delay in setting, it is necessary that these experiments should be carried out under uniform conditions of heating as to air, water, and cement, in order to obtain corresponding results, and the mean temperatures should range between 15° and 18° Centigrade (59° to 64·4° Fahrenheit), and the vessels and sand should previously be brought to this same temperature.

The opinion that Portland cement loses its strength by long storage is erroneous ; so long as the Portland cement is kept dry and free from draught. Contract clauses which prescribe the delivery only of freshly made cement should be deleted.

4. **Constancy of Volume.**—Portland cement must be constant in volume. The decisive test for this purpose shall be that a pat of neat cement, prepared on a glass plate and protected from too rapid drying, immersed in water at the end of 24 hours and kept under constant observation for a further period shall manifest no tendency to curl up or become cracked at the edges.

*Explanation.*—In carrying out this test the pat used to determine the setting time should, after 24 hours in the case of slow-setting cement, but at any rate only after the cement has become completely set, be placed in water. In the case of quick-setting cements this may take place after an even shorter interval. The pats of slow-setting Portland cements must, until the setting process is complete, be protected from rapid drying ; for which purpose they may best be placed in a covered box. By this means, the formation of hair-cracks due to speedy drying, which generally appear in the centre of the pat, may be avoided : such cracks are sometimes mistaken by unskilled observers for cracks caused by blowing.

If during the process of induration under water, curling up, or cracking at the edges becomes manifest, it denotes undoubtedly the blowing of the Portland cement—that is to say, that, in consequence of its volumetric expansion, the cement becomes cracked, owing to gradual disintegration of the original cohesion of the mass, which may lead to the total disruption of the cement.

The appearances due to blowing generally become apparent in the pats after about three days' time, but at all events observations over a period of 28 days are sufficient.

5. **Fineness of Grinding.**—Portland cement must be ground sufficiently fine so that the residue on a sieve of 900 meshes per square centimetre (5,806 per square inch or 76 per lineal inch) does not exceed 5 per cent. The width of the mesh should be 0·222 millimetre (0·00874 inch).

BASIS AND EXPLANATION.

For the sieve test 100 grammes (0·22 lb.) of Portland cement are to be used.

Accurate sieves cannot be obtained commercially, and, therefore, fluctuations between 0·215 mm. and 0·240 mm. (0·00828 inch and 0·00984 inch) are permissible in the width of mesh.

As cement is almost invariably employed with sand, and in many cases with large additions of sand, the strength of the mortar is greater the finer the cement used with it is ground (because under these circumstances more particles of cement come into action), it is, therefore, important that the cement should be finely ground. It would, however, be misleading to judge of the quality of a cement only by the fineness of the grinding.

6. **Strength Tests.**—Portland cement is to be tested for compressive strength in the form of a mixture of cement and sand, made upon a uniform principle and in the shape of cubes with a face area of 50 square centimetres (7·75 square inches).

· *Basis.*—Because it is not possible to judge uniformly of the capacity of the cement for uniting sand particles by means of tests, conducted with neat cement—namely, when it is necessary to compare samples of cement obtained from different factories—it is laid down that the testing of the cohesion of the cement should take place when mixed with sand.

Because, in the use of mortar, the chief essential is the compressive strength, and this can best be the subject of test, the only decisive test is that under compression.

In order to guarantee the requisite degree of uniformity in the testing, it is recommended that the apparatus and tools used for testing should be the same as those employed at the State Office for the Testing of Materials at Gross Lichterfelde.

7. **Strength.**—Slow-setting Portland cement, made up with 3 parts by weight of normal sand and 1 part by weight of cement. must after a period of seven days—one day in moist air and six days under water—attain a strength of at least 120 kilogrammes per square centimetre (1,706·76 lbs. per square inch) preliminary test; after a further period of 21 days kept in air, at a room-temperature of 15° to 20° C. (59° to 68° F.), the strength in compression must attain at least 250 kilogrammes per square centimetre (3,555·75 lbs. per square inch). In case of controversy only the test after 28 days is decisive.

Portland cement for use in water, after 28 days' setting time—1 day in moist air and 27 days under water—must have a strength under compression of at least 200 kilogrammes per square centimetre (2,844·64 lbs. per square inch).

In order to facilitate the testing on the work, a tensile test may be adopted.

The cement mixture made up with 1 part of cement to 3 parts of normal sand after seven days' induration (one day in air and six days in water) must show at least 12 kilogrammes per square centimetre (170·67 lbs. per square inch).

In the case of quick-setting Portland cements, the tensile strength after 28 days is generally less than that above laid down. It is, therefore, necessary, in stating the requisite tensile strength, to give the period needed for setting.

### Basis and Explanation.

As different kinds of Portland cement, in respect of their power of uniting sand, which is their main use in practice, may behave in very various ways, it is especially necessary in comparing several kinds of Portland cement to carry out the test with large proportions of sand. The normal proportion laid down is 3 parts of sand to 1 part of Portland cement, because with 3 parts of sand it is possible to ascertain the exact capabilities of various kinds of cement as respects their power of uniting sand.

When, however, the ultimate properties of a sample of cement need to be fully demonstrated, it is advisable to conduct a series of tests with larger proportions of sand.

Portland cement which shows a high degree of strength will, in many cases, allow of a larger addition of sand, and is entitled from this point of view, as also on account of its greater strength with an equal amount of sand, to be sold at a higher price.

As by far the greater amount of Portland cement is employed for building purposes, and fails to develop its full binding power in a short interval of time, the essential test is regarded as that under compression after induration for 28 days—one day in moist air and six days under water—and then 21 days in air at the ordinary temperature of the room, 15° to 20° C. (59° to 68° F.), and this is convenient for practical purposes.

In the case of cement for structures in water, the test of 27 days' induration under water is laid down in accordance with the practical use of the material. Because it is not always possible to deduce from the tensile strength of the cement the corresponding strength under compression, it is advisable when the tensile strength at seven days is very high to test the cement specially also in compression. In order to obtain uniform results, it is necessary, in all cases, to use sand with the same size of grains and of the same quality (normal sand). The German normal sand is procured from a tertiary deposit of quartz of the lignite beds in the vicinity of Frienwalde a Oder. The nearly white raw sand is washed in a special machine and dried. The sifting of the sand takes place in rocking sieves which are suspended in pendulum fashion. By means of one sieve the coarse particles are removed,

and then on a second the fine grains. A sample of each day's production is sent to the State Testing Station, Gross Lichterfelde, for test of size of grain and purity.

The measurement of the size of sand grain is ascertained by means of sieves of brass plate, 0·25 mm. (0·0098 inch) in thickness, with circular holes of a diameter of 1·350 and 0·775 mm. (0·0531 and 0·0305 inch) respectively.

Normal sand found after repeated tests to be satisfactory is put into sacks, each of which bears the seal of the State Testing Station.

**Description of the Test to Ascertain the Strength.**—In order to ensure that the testing of the same sample of cement at different places may give rise to corresponding results, special care must be taken to comply exactly with the rules hereafter laid down. In order to attain correct average results, at least five test-pieces must be made of each sample.

*Translator's Note.*—Very precise instructions are laid down for the preparation of the normal cement mortar, with 3 sand to 1 cement, and for the moulding of the test-pieces, with the details of the apparatus to be employed for this purpose, comprising the Steinbruck-Schmelze's mixing machine, the moulding frames for the cubes, the Bohme hammer, the Vicat needle, the Martens' moulding plant, the Amsler-Laffan mercurial press, etc.

Special directions are likewise included for the delivery of the cement, and concerning the steps to be taken in case of disputes as to quality. These details have not been added to the present translation.


## A FRENCH (Schedule of Charges) SPECIFICATION.*

## MINISTRY OF PUBLIC WORKS.

### Ministerial Decree concerning Deliveries of Cements and Hydraulic Limes.

ARTICLE 1.

**General Regulations.**—All deliveries of cement and lime relating to the execution of works required for the administration of Public Works, whether it is a question of contracts for the supply without actual use of the materials, or for contracts involving their employment (in construction) are subject to the following conditions, so far as they may be applicable :—

FIRST SCHEDULE.

Clauses applicable to all contracts.

* Translation by Gilbert R. Redgrave.

## ARTICLE 2.

**Mode of Delivery.**—The cement and the lime, where the latter is furnished in powder, are to be delivered in bags or in casks. The bags must contain a net weight of 50 kilogrammes (110·12 lbs.) ; they must be stitched inside, and must be fastened with a leaden seal, bearing the mark of the manufacturer, of a pattern approved by the administration.*

The casks must be stamped on one end with the mark of the manufacturer, and on the other with the net weight contained of lime or cement.

The sacks and casks must be in perfect condition at the time of delivery. All moist cement or lime will be rejected.

On the delivery of each consignment, the invoices or carting tickets must be submitted to the Engineer.

## ARTICLE 3.

**Storage.**—The sacks or casks of cement or of lime must be stored in very dry, closed, and covered sheds. They must be arranged in distinct lots corresponding with each separate delivery.

The contractor will undertake the charge of and be responsible for the cements and limes in stores, up to the moment of use, except in the case stipulated under Article 17.

Every sack or cask of cement or lime found to be damaged, or with the casing in a defective condition, at the time it is required for use, will be rejected.

## ARTICLE 4.

**Tests.**—No cement or lime can be used in the work before it has undergone the tests laid down in the special specification relating to the contract, and has been provisionally accepted.

The engineer shall be entitled to remake, at any time during the whole period that the limes or cements, which have been accepted provisionally, remain in the store, the tests laid down in the specification, and to reject those consignments which at the time they are to be used fail to comply with the requirements specified.

When the tests have proved unfavourable, the contractor has the right to demand that they may be repeated in the laboratory of the Engineering School.

## ARTICLE 5.

**Taking the Samples.**—The samples for testing shall be taken at two different depths, and at various points, from several sacks, casks, or bins

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* See the modification, introduced by Ministerial Decree of November 9, 1909, in respect of lime under Schedule 2.

pointed out by the engineer. The cements or limes included under different consignments must not be mixed.

## ARTICLE 6.

**Quality.**—The cement or the lime must be uniform in composition and constant in quality ; they must be free from underburned particles and foreign matters.

## ARTICLE 7.

**Fineness of Grinding and Screening.**—The samples must consist of 100 grammes in weight. The sieves must contain respectively 324, 900, and 4,900 meshes to the square centimetre. The wires used for the three sieves must be of the respective sizes of 20, 15, and 5 hundredths of a millimetre in diameter.

## ARTICLE 8.

**Apparent Density.**—The apparent density shall be determined by slowly pouring the cement or the lime, without causing its compression, into a metal vessel of cylindrical form, ten centimetres in height, holding 1 litre. The cement, or the lime, contained in this measure shall be weighed. The apparent density shall be the mean result of the weights of three successive fillings.

In case of a dispute, the filling of the measure shall be effected by means of a metal funnel sieve perforated with holes 2 millimetres in diameter. This funnel must be fixed so that it shall deliver at a height of 5 centimetres above the top of the measuring vessel. The cement, or the lime, shall be poured in with the avoidance of any shock or shaking. When the measure is filled, the superfluous material shall be scraped level by means of a blade held upright passed across its surface.

## ARTICLE 9.

**Time of Setting.**—The cement, or the lime, shall be gauged with potable water to a stiff paste, and shall, after being made into pats about 4 centimetres in thickness, be placed immediately in potable water or in sea water, in accordance with the conditions laid down in the specification relating to the work. The cement, or the lime, the water used in gauging, and the bath into which the samples are laid, shall have a temperature of at least 15° C. (59° F.), when it is a question of deciding the rapidity of test, and of 15° at the utmost when the minimum speed of set is to be determined.

The period of initial setting time shall be taken as that when the Vicat

needle, with a section of 1 square millimetre, and a weight of 300 grammes, fails to penetrate through the entire thickness of the pat.

The period of complete set shall be defined as that when the surface of the cake will no longer permit the same needle to penetrate it to any notable extent, beyond, say, the tenth part of a millimetre.

In case of dispute, a stiff paste of cement or lime shall be considered to be one mixed up for five minutes per kilogramme, and then placed in a vessel having a depth of 4 centimetres, which shall be penetrated to within 6 millimetres of the bottom of the vessel by a wire sound (or needle) with a diameter of 1 centimetre, loaded with 300 grammes.

## ARTICLE 10.

**Resistance to Tension.**—The tests for resistance may be carried out with stiff paste of cement or pure lime, or with plastic mortar of cement or of lime gauged with potable water. They are to be carried out by means of test-pieces in the form of a figure of 8, having a section at the neck of 5 square centimetres.*

The moulds for making the test-pieces must be filled at one operation ; they are to be carefully shaken to expel the air bubbles ; the paste or mortar may then be squeezed in with the trowel and pressed down, but not wedged or rammed, after which the surplus material may be scraped off level with top of mould with the edge of the trowel and the surface may be smoothed over.

Each test will be carried out with six test-pieces. The resistance to tension will be the mean of the four best results.

The mortar is to be composed of 1 part of cement or lime to 3 parts of dry sand—the sand is to consist of equal parts of grains of three different sizes, separated by means of four metal sieves perforated with holes of $\frac{1}{2}$, 1, $1\frac{1}{2}$, and 2 millimetres in diameter.

The test-pieces, after having been kept in a moist atmosphere, and sheltered from air currents and from the sun, for the time laid down in the specification, shall be removed from the moulds and placed in potable water or sea water, in accordance with the terms of the specification. In any case the water is to be renewed every seven days.

In case of dispute, a stiff paste of cement or of pure lime shall be considered such as is defined under Article 9, and a plastic mortar of cement or of lime shall be a mortar made up with sand taken from the coast at Leucate, furnished by the administration, and gauged with a volume of water equal for 1 kilogramme of material to 70 grammes + $\frac{1}{6}$P, P being the requisite weight needed to transform 1 kilogamme of cement or of lime into stiff paste.

* 55 grammes + $\frac{1}{6}$ of weight (P), Circular of Nov. 20, 1904.

## ARTICLE 11.

**Deformations due to Cold or Heat.**—The tests for changes caused by cold are to be made with pats of cement or of lime, gauged into a stiff paste with potable water. The pats are to be about 10 centimetres in diameter and 2 centimetres thick in centre, but thinned out towards the edge and made up on glass plates. The pats are to be immersed in water under the conditions attached to the special specification and kept in water until the final reception of the cement or of the lime. Not one of the pats must present the least trace of swelling, extending outwards, or general expansion. The edge of the pat must remain well affixed to the glass plate, and must not lift at any part.

The test for changes caused by heat must be carried out by means of cylindrical test-pieces, with diameter and altitude each equal to 30 millimetres, moulded in a brass tube $\frac{1}{2}$ millimetre in thickness, split up round a core and having soldered at each side of the slit a needle 150 millimetres in length.

In the twenty-four hours following the completion of the set, these test-pieces are to be immersed in water, which is to be progressively heated to the temperature fixed by the specification, and maintained at this temperature for a time likewise provided for by the specification in question, and then cooled down to the initial temperature. The increase in the space between the needles' points must not exceed the amount laid down in this special specification.

None of the pats and test-pieces must show the least signs of swelling, such as cracks, expansion, or disruption. The edges of the pats must remain well attached to the glass plate, and must not lift at any point.

## ARTICLE 12.

**Constancy of Temperature.**—The water in which the test-pieces and pats are immersed must be kept at a temperature between 12° and 18° Centigrade (54° and 64° Fah.).

## ARTICLE 13.

**Removal of Rejected Cement and Lime.**—The cement and lime rejected must be removed from the store under the care of and at the cost of the contractor within a period of ten days from the date of the official notification or rejection.

In default of compliance by the contractor with this regulation, the engineer may proceed to cause the removal of the rejected cement or lime, and this cement or lime shall be carried away and placed in a warehouse hired for the purpose at the cost, risk, and peril of the contractor.

## SCHEDULE II.

### Clauses applicable to Contracts for Deliveries when Material is not used by Contractor.

ARTICLE 14.

**Orders.**—The cement or the lime must be delivered in successive lots, the amounts of which, and the intervals between the order and delivery, will be fixed by the orders given. The special specification for the work will determine the maximum quantities of cement or of lime which may be required each month from the contractor, as also the minimum period allowed for the completion of each order.

In case of delay in delivery, the administration can, ten days after due notification to the contractor of a compulsory order by the engineer, buy on their own account and at the contractor's cost, the quantities of cement or lime that he has failed to deliver.

If the cement or the lime supplied has entailed legal notice of rejection, and the contractor in receipt of a compulsory order has not replaced within the time specified by the engineer, which must be not less than ten days, the cement or the lime rejected, the administration is entitled to buy on their own behalf, and at the cost of the contractor, an amount of cement or of lime equal to that which has been rejected.

In these two cases, the amount of the contract shall be diminished by these sums without enabling the contractor to claim the benefits of Article 31 of the General Clauses and Conditions.

ARTICLE 15.

**Return of Packages.**—Empty sacks are to be returned to the warehouse at the Administrative Office, at the time and place of use, and are to be entrusted to the contractor, who is under obligation to take them away at his own cost.

In default of their removal within the period fixed by the engineer, and in case the stock becomes excessive, so as to cause encumbrance in the stores, empty sacks will be returned to the contractor officially to his yard and at his expense.

The value of the sacks not returned is to be paid by the contractor, at the conclusion of the contract, in accordance with the price laid down in the schedule, without deduction of the rebate arranged by the adjudicators.

Empty cement casks remain the property of the State.

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ARTICLE 16.

**Weighing (of Goods).**—All the sacks or casks shall be weighed as a check on accuracy at the moment of being received at the warehouse.

The tare weight is to be determined by weighing a number of packages equivalent to 10 per cent. approximately of the total number.

ARTICLE 17.

**Reception (of Goods).**—The provisional receipt of each consignment of goods shall be declared as soon as the cement or lime, composing such delivery of goods, has been found to comply with the tests laid down in the specification for the contract.

The cement or the lime thus provisionally received shall be taken into account as materials on hand up to the time of their actual use on the job.

The cement or the lime, which has not been actually used within a period of six months after the provisional receipt, shall be regarded as forming a part of the finished work, on the expiration of the term of six months, if they have complied with all the conditions laid down, and the contractor shall thereupon be released from all responsibility for the due care and warehousing of the goods.

ARTICLE 18.

**Period of Guarantee.**—The period over which the guarantee extends shall amount to one year, dating from the provisional receipt of the last partial consignment of goods.

THE MINISTER OF PUBLIC WORKS.

(Signed)    PIERRE BAUDIN.

PARIS, *June* 2, 1902.

**SPECIFICATION, Type 1, for the Supply of PORTLAND CEMENT for Works to be executed in Sea Water (Circular of June 2, 1902).**

ARTICLE 1.

**Description of Product.**—The Portland cement must be produced by grinding an intimate mixture of carbonate of lime, silica, alumina, and iron, calcined to incipient fusion.

ARTICLE 2.

**Place of Manufacture and Inspection at the Factory.**—The cement shall come directly and exclusively from  ·.  .  .  (1).

(1) If the material is to be supplied only for stock—give the makers' name.

If the material is supplied for building operations, and if the state or nature of the works is such as to warrant the mention of the origin of the cement, state "from one of the factories named herein."

If the contract comprises the supply for building operations, for which it is not necessary to state exactly the origin of the cement, insert the words "from the factory chosen by the contractor and approved by the engineer."

The authorities reserve to themselves the right to exercise their control at the factory, not only over the actual manufacture, but also of the storage and despatch of the cement furnished in execution of the present specification.

Special agents may be appointed permanently for this purpose.

## ARTICLE 3.

**Mode of Delivery.**—The cement shall be delivered in sacks or in casks.

## ARTICLE 4.

**Chemical Composition.**—The cement must not contain more than 1·5 per cent. of sulphuric acid, nor more than 2 per cent. of magnesia, nor more than 8 per cent. of alumina, nor more than traces of sulphides.

The hydraulic index—that is to say, the ratio between the weight of the combined silica and the alumina in the first place, as against the weight of the lime and magnesia in the second place—shall be at least 0·47 for a proportion of 8 per cent. of alumina, with a diminution of 0·02 for each 1 per cent. of alumina below 8 per cent.

## ARTICLE 5.

**Fineness of Grinding.**—The cement must leave at least 40 per cent. of its weight on a sieve with 4,900 meshes per square centimetre (about 31,000 per square inch), and at most 2 per cent. on a sieve of 324 meshes (about 1,990 per square inch).

## ARTICLE 6.

**Apparent Density.**—The weight of a litre of cement shall be at least 1,200 grammes.

## ARTICLE 7.

**Setting Time.**—The cement immersed in potable water must not begin to show signs of setting in less than 20 minutes.

The complete set must be effected in a period of not less than 3 hours or more than 12 hours.

## ARTICLE 8.

**Tensile Strength of Neat Cement.**—The test-briquettes of neat cement, immersed in sea water at the end of 24 hours, must show a tensile strength of at least 15 kilogrammes per square centimetre after 7 days (213·3 lbs. per square inch), and 30 kilogrammes after 28 days (426·6 lbs. per square inch).*

The gain in strength must be at least 2 kilogrammes (28·44 lbs.) from the 7th to the 28th day.

## ARTICLE 9.

**Tensile Strength of Cement Mortar.**—The test-briquettes of cement mortar, immersed in sea water at the end of 24 hours, must show a tensile strength of at least 6 kilogrammes per square centimetre after 7 days (85·3 lbs. per square inch) and 12 kilogrammes † after 28 days (170·6 lbs. per square inch).‡

The strength must anyhow increase at least 2 kilogrammes (28·44 lbs.) from the 7th to the 28th day.

## ARTICLE 10.

**Changes in Form due to Cold and Heat.**—The pats and test pieces are to be kept in a moist atmosphere for 24 hours ; the pats are then at once to be immersed in sea water. The temperature for the heat test to bring about change in form shall be 100° Cent. (212° Fah.), and is to be maintained for 3 hours. The bulk extension as shown by the needle-points (Le Châtelier apparatus) must not exceed 5 millimetres ($\frac{1}{5}$ inch).

## SPECIFICATION, Type 2, for the Supply of Hydraulic Lime for Use in Works executed in Sea Water (Circular of June 2, 1902).

## ARTICLE 1.

**Description of the Material.**—The lime is to be delivered in a finely powdered state, free from imperfectly calcined particles and from all extraneous matter.

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* The above are minimum figures, and the engineer may increase them if he is certain that the factory is capable of supplying cement which will stand the higher tests.
† Subsequently altered to 11 kilogrammes (156·4 lbs. per sq. in.).
‡ The same remark as in the case of Article 8.

## ARTICLE 2.

**Place of Manufacture and Inspection at the Factory.**—The lime shall come directly and exclusively from . . . *.

The authorities reserve to themselves the right to exercise their control at the factory, not only of the actual manufacture, but also with respect to the storage and delivery of the lime supplied in execution of the present contract.

Special agents may be appointed permanently for this purpose.

## ARTICLE 3.

**Mode of Delivery.**—The lime may be delivered in sacks or in casks.

## ARTICLE 4.

**Chemical Composition.**—The lime must contain less than 2 per cent. of alumina, more than 20 per cent. of combined silica, and must not lose more than 10 per cent. of its weight when heated to bright redness.

These figures are not obligatory in the case of limes which have undergone satisfactorily the tests in the sea, carried out by the Commission on Limes and Cements, at the request of manufacturers who may desire to submit their materials for tenders for sea works.

## ARTICLE 5.

**Fineness of Grinding.**—The lime must not leave more than 5 per cent. of its weight on the sieve with 900 meshes per square centimetre (5,805 meshes per square inch) nor more than 2 per cent. on the sieve of 324 meshes (about 1,990 per square inch).

## ARTICLE 6.

**Apparent Density.**—The weight of the litre of lime must be in excess of 700 grammes. In the case of limes coming from the same factory, the variations in the weight per litre must not exceed 100 grammes.

## ARTICLE 7.

**Setting Time.**—The lime made up into paste and immersed in sea water must show signs of initial set within a period of 6 hours, and must become completely set in a period of 30 hours at most.

* Same conditions as those laid down in the case of Portland cement (pp. 370 and 371).

ARTICLE 8.

**Tensile Strength of Lime Mortar.**—The test-briquettes of mortar immersed in sea water at the end of 24 hours must have a tensile strength of 3 kilogrammes per square centimetre (42·66 lbs. per square inch) at the end of 7 days and 6 kilogrammes per square centimetre (85·32 lbs. per square inch) at the end of 28 days.*

The gain in strength from the 7th to the 28th day must be at least 2 kilogrammes (28·44 lbs.).

ARTICLE 9.

**Changes in Form due to Cold and Heat.**—The pats and test pieces shall be kept in a moist atmosphere for 24 hours, and shall then be immersed in sea water. The temperature for the heat test of the pats shall be 100° C. (212° F.), and shall be maintained for 3 hours.

The increase in width between the points of the needles must not exceed 5 millimetres (about ⅕ inch).

**SPECIFICATION, Type 3, for the Supply of Portland Cement destined for Works not to be carried out in Sea Water (Circular of June 2, 1902).**

ARTICLE 1.

**Description of Product.**—The Portland cement must be produced by grinding an intimate mixture of carbonate of lime, silica, alumina, and iron calcined to incipient fusion.

ARTICLE 2.

**Place of Manufacture and Inspection at the Factory.**—The cement shall come directly and exclusively from . . . †.

The authorities reserve to themselves the right to exercise their control at the factory, not only over the actual manufacture, but also of the storage and despatch of the cement furnished in execution of the present contract.

Special agents may be appointed permanently for this purpose.

ARTICLE 3.

**Mode of Delivery.**—The cement may be delivered in sacks or in casks.

* These are minimum figures. Engineers may increase them if they are satisfied that the factories can supply materials capable of undergoing the more severe tests.
† Conditions as before, see pp. 370 and 371.

## ARTICLE 4.

**Chemical Composition.**—The cement must not contain more than 3 per cent. of sulphuric acid, nor more than 5 per cent. of magnesia, nor more than 10 per cent. of alumina, with only traces of sulphides.

## ARTICLE 5.

**Fineness of Grinding.**—The cement must not leave more than 30 per cent. of its weight on the sieve of 4,900 meshes per square centimetre (about 31,000 per square inch), nor more than 10 per cent. on the sieve with 900 meshes (about 5,806 meshes per square inch).

## ARTICLE 6.

**Apparent Density.**—The weight of a litre of cement must be at least 1,100 grammes.

## ARTICLE 7.

**Setting Time.**— The cement immersed in potable water must not begin to show signs of setting in less than 20 minutes.

The complete set must be effected in a period of not less than 2 hours nor more than 12 hours.

## ARTICLE 8.

**Tensile Strength of Neat Cement.**—The test-briquettes of neat cement immersed in potable water at the end of 24 hours must show a tensile strength of at least 25 kilogrammes per square centimetre (375 lbs. per square inch) after 7 days, and 35 kilogrammes after 28 days (497·8 lbs. per square inch).*

The gain in strength must be at least 3 kilogrammes (42·66 lbs.) from the 7th to the 28th day.

## ARTICLE 9.

**Tensile Strength of Cement Mortar.**—The test-briquettes of cement mortar immersed in potable water at the end of 24 hours must show a tensile strength of at least 8 kilogrammes per square centimetre (113·7 lbs. per square inch), and 15 kilogrammes (213·3 lbs.) at the end of 28 days.†

The gain in strength must be at least 2 kilogrammes (28·4 lbs.) from the 7th to the 28th day.

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* The above are minimum figures, and the Engineer may increase them if he is certain that the factory is capable of supplying cement which will stand the higher tests.

† Same observations as in the case of Article 8.

ARTICLE 10.

Changes caused by Heat.—The test-briquettes must be kept in a moist atmosphere for 24 hours. The temperature for the heat test is to be 100° C. (212° F.), and is to be maintained for 3 hours. The increase in the space between the points of the needles must not exceed 10 millimetres ($\frac{2}{5}$ inch).

SPECIFICATION, Type 4, for the Supply of " Grappiers " Cement (Circular of June 2nd, 1902).

ARTICLE 1.

Description of the Material.—Grappiers cement is to be produced by grinding the grappiers (lime ashes), forming the residue of highly calcined limes, separated from the lime by quenching and repeated screening operations.

ARTICLE 2.

Place of Manufacture and Inspection at the Factory.—The cement shall come directly and exclusively from . . . (1).

(1) If the material is to be supplied only for stock, give the makers' name.

If the material is supplied for building operations, and if the state or nature of the works is such as to warrant the mention of the origin of the cement, give " from one of the factories named herein."

If the contract comprises the supply for building operations for which it is not necessary to state exactly the origin of the cement, insert the words, " from the factory chosen by the contractor and approved by the engineer."

The authorities reserve to themselves the right to exercise their control at the factory, not only over the actual manufacture, but also of the storage and despatch of the cement furnished in execution of the present specification.

Special agents may be appointed permanently for this purpose.

ARTICLE 3.

Mode of Delivery.—The cement shall be delivered in sacks or in casks.

ARTICLE 4.

Chemical Composition.—The cement must not contain more than 1·5 per cent. of sulphuric acid nor more than 5 per cent. of magnesia, nor more than 22 per cent. of combined silica. If the cement is destined for use in

works in sea water, it should moreover be laid down that it must not contain more than 3 per cent. of alumina.

These figures are not obligatory in the case of cements which have undergone satisfactorily the tests carried out by the Commission on Limes and Cements at the request of manufacturers who may desire to submit their materials in tenders for public works.

## ARTICLE 5.

**Fineness of Grinding.**—The cement should not leave more than 30 per cent. of its weight on the sieve of 4,900 meshes per square centimetre (about 31,000 per square inch), nor more than 10 per cent. on the sieve with 900 meshes (about 5,806 meshes per square inch).

## ARTICLE 6.

**Setting Time.**—The cement immersed in potable water must have commenced to become set within a period of 5 hours, and must have set completely in 14 hours.

## ARTICLE 7.

**Tensile Strength of Cement Mortar.**—The test-briquettes of work immersed in potable water at the end of 24 hours must have a tensile strength of 8 kilogrammes per square centimetre (113·76 lbs. per square inch) at the end of 7 days, and 12 kilogrammes (170·64 lbs. per square inch) at the end of 28 days.*

If the cement is intended for use in sea water the tensile strength required at 7 and 28 days shall be respectively 10 and 15 kilogrammes (142·2 lbs. and 213·3 lbs. per square inch). There must further be a gain in strength between the 7th and 28th day.

## ARTICLE 8.

**Change in Form due to Cold and Heat.**—The pats and test-pieces shall be kept in .a moist atmosphere for 24 hours. The temperature for the heat test of the pats shall be 100° C. (212° F.), and shall be maintained for 3 hours. The increase in width between the points of the needles must not exceed .5 millimetres (⅕ inch) in the case of materials for use in sea works, and 10 millimetres (⅖ inch) for other work.

* The above are minimum figures. Engineers may increase them if they are satisfied that the factories can supply materials capable of undergoing a more severe test.

*(Addition to the Circular of November 9th, 1909.)*

**SPECIFICATION, Type 6, for the Supply of Hydraulic Lime not intended for Works in Sea Water.**

ARTICLE 1.

**Mode of Delivery.**—The lime must be delivered in powder and enclosed in sacks, the leaden seals of which will guarantee the quality. They will bear the mark, " Hydraulic, 1 Category, No. 6."

ARTICLE 2.

**Place of Manufacture.**—The lime comprised in each delivery shall always be the product of one and the same works.

ARTICLE 3.

**Fineness of Grinding.**—The lime must leave not more than 5 per cent. of its weight on the sieve of 900 meshes per square centimetre (5,805 meshes per square inch), nor more than 25 per cent. on the sieve of 4,900 meshes per square centimetre (about 31,000 per square inch).

ARTICLE 4.

**Setting Time under Water.**—The lime paste, immersed in potable water, must begin to become set before the expiration of 24 hours.

ARTICLE 5.

**Tensile Strength of the Lime Mortar.**—The test-briquettes of mortar removed from the moulds at the end of 24 hours and then immersed in potable water after 48 hours must show a strength of 2·5 kilogrammes per square centimetre (35·55 lbs. per square inch) after 7 days, and 6 kilogrammes (71·1 lbs. per square inch) after 28 days.

ARTICLE 6.

**Change in Form due to Heat.**—The cylindrical test-pieces must be kept in a moist atmosphere for 48 hours and then immersed in potable water. The test for change of form is to be carried out 4 days after gauging. The temperature for the heat test is to be 100° C. (212° F.). It is to be maintained for 3 hours. The alteration in width between the points of the needles must not exceed 10 millimetres (⅖ inch).

All lime which shall have expanded appreciably before the heat test shall be rejected.

# Report of a Committee of the American Society for Testing Materials on a Standard Specification for Cement.

## STANDARD SPECIFICATIONS FOR CEMENT.

1. **General Observations.**—These remarks have been prepared with a view of pointing out the pertinent features of the various requirements and the precautions to be observed in the interpretation of the results of the tests.

2. The committee would suggest that the acceptance or rejection under these specifications be based on tests made by an experienced person having the proper means for making the tests.

3. **Specific Gravity.**—Specific gravity is useful in detecting adulteration or underburning. The results of tests of specific gravity are not necessarily conclusive as an indication of the quality of a cement, but when in combination with the results of other tests may afford valuable indications.

4. **Fineness.**—The sieves should be kept thoroughly dry.

5. **Time of Setting.**—Great care should be exercised to maintain the test pieces under as uniform conditions as possible. A sudden change or wide range of temperature in the room in which the tests are made, a very dry or humid atmosphere, and other irregularities vitally affect the rate of setting.

6. **Tensile Strength.**—Each consumer must fix the minimum requirements for tensile strength to suit his own conditions. They shall, however, be within the limits stated.

7. **Constancy of Volume.**—The tests for constancy of volume are divided into two classes—the first normal, the second accelerated. The latter should be regarded as a precautionary test only, and not infallible. So many conditions enter into the making and interpreting of it that it should be used with extreme care.

8. In making the pats the greatest care should be exercised to avoid initial strains due to moulding or to too rapid drying-out during the first twenty-four hours. The pats should be preserved under the most uniform conditions possible, and rapid changes of temperature should be avoided.

9. The failure to meet the requirements of the accelerated tests need not be sufficient cause for rejection. The cement may, however, be held for twenty-eight days, and a re-test made at the end of that period. Failure to meet the requirements at this time should be considered sufficient cause for rejection, although in the present state of our knowledge it cannot be said that such failure necessarily indicates unsoundness, nor can the cement be considered entirely satisfactory simply because it passes the tests.

STANDARD SPECIFICATIONS FOR CEMENT.

1. **General Conditions.**—All cement shall be inspected.

2. Cement may be inspected either at the place of manufacture or on the work.

3. In order to allow ample time for inspecting and testing, the cement should be stored in a suitable water-tight building having the floor properly blocked or raised from the ground.

4. The cement shall be stored in such a manner as to permit easy access for proper inspection and identification of each shipment.

5. Every facility shall be provided by the contractor, and a period of at least twelve days allowed for the inspection and necessary tests.

6. Cement shall be delivered in suitable packages with the brand and name of manufacturer plainly marked thereon.

7. A bag of cement shall contain 94 lbs. of cement net. Each barrel of Portland cement shall contain four bags, and each barrel of natural cement shall contain three bags of the above net weight.

8. Cement failing to meet the seven-day requirements may be held awaiting the results of the twenty-eight-day tests before rejection.

9. All tests shall be made in accordance with the methods proposed by the Committee on Uniform Tests of Cement of the American Society of Civil Engineers, presented to the Society, January 21, 1903, and amended January 20, 1904, with all subsequent amendments thereto. (See addendum to these specifications.)

10. The acceptance or rejection shall be based on the following requirements :—

NATURAL CEMENT.

11. **Definition.**—This term shall be applied to the finely pulverised product resulting from the calcination of an argillaceous limestone at a temperature only sufficient to drive off the carbonic acid gas.

12. **Specific Gravity.**—The specific gravity of the cement thoroughly dried at 100° C. shall be not less than 2·8.

13. **Fineness.**—It shall leave by weight a residue of not more than 10 per cent. on the No. 100, and 30 per cent. on the No. 200 sieve.

14. **Time of Setting.**—It shall develop initial set in not less than ten minutes, and hard set in not less than thirty minutes, nor more than three hours.

15. **Tensile Strength.**—The minimum requirements for tensile strength for briquettes 1 inch square in cross-section shall be within the following limits, and shall show no retrogression in strength within the periods specified :—

NEAT CEMENT.

| Age. | | | | | | | Strength. |
|---|---|---|---|---|---|---|---|
| 24 hours in moist air, | . | . | . | . | . | . | 50-100 lbs. |
| 7 days (1 day in moist air, 6 days in water), | . | | . | | . | . | 100-200 ,, |
| 28 ,, (1 ,, 27 ,, ), | . | | . | | . | . | 200-300 ,, |

ONE PART CEMENT, THREE PARTS STANDARD SAND.

| | | | | | Strength. |
|---|---|---|---|---|---|
| 7 days (1 day in air, 6 days in water), | . | . | . | . | 25- 75 lbs. |
| 28 ,, (1 ,, 27 ,, ), | . | . | . | . | 75-150 ,, |

16. **Constancy of Volume.**—Pats of neat cement about 3 inches in diameter, ½ inch thick at centre, tapering to a thin edge, shall be kept in moist air for a period of twenty-four hours.

(*a*) A pat is then kept in air at normal temperature.

(*b*) Another is kept in water maintained as near 70° F. as practicable.

17. These pats are observed at intervals for at least twenty-eight days, and, to satisfactorily pass the tests, should remain firm and hard and show no signs of distortion, checking, cracking, or disintegrating.


PORTLAND CEMENT.

18. **Definition.**—This term is applied to the finely-pulverised product resulting from the calcination to incipient fusion of an intimate mixture of properly proportioned argillaceous and calcareous materials, and to which no addition greater than 3 per cent. has been made subsequent to calcination.

19. **Specific Gravity.**—The specific gravity of the cement, thoroughly dried at 100° C., shall be not less than 3·10.

20. **Fineness.**—It shall leave by weight a residue not more than 8 per cent. on the No. 100, and not more than 25 per cent. on the No. 200 sieve.

21. **Time of Setting.**—It shall develop initial set in not less than thirty minutes, but must develop hard set in not less than one hour, nor more than ten hours.

22. **Tensile Strength.**—The minimum requirements for tensile strength for briquettes 1 inch square in section shall be within the following limits, and shall show no retrogression in strength within the periods specified :- -

NEAT CEMENT.

| Age. | | | | | | | Strength. |
|---|---|---|---|---|---|---|---|
| 24 hours in moist air, | . | . | . | . | . | . | 150-200 lbs. |
| 7 days (1 day in moist air, 6 days in water), | . | | . | | . | . | 450-550 ,, |
| 28 ,, (1 ,, 27 ,, ), | . | | . | | . | . | 550-650 ,, |

ONE PART CEMENT, THREE PARTS SAND.

| | | | | | Strength. |
|---|---|---|---|---|---|
| 7 days (1 day in moist air, 6 days in water), | . | . | . | . | 150-200 lbs. |
| 28 ,, (1 ,, 27 ,, ), | . | . | . | . | 200-300 ,, |

23. **Constancy of Volume.**—Pats of neat cement about 3 inches in diameter, $\frac{1}{2}$ inch thick at the centre, and tapering to a thin edge, shall be kept in moist air for a period of twenty-four hours.

(a) A pat is then kept in air at normal temperature and observed at intervals for at least twenty-eight days.

(b) Another pat is kept in water maintained as near 70° F. as practicable, and observed at intervals for at least twenty-eight days.

(c) A third pat is exposed in any convenient way in an atmosphere of steam, above boiling water, in a loosely-closed vessel for five hours.

24. These pats, to satisfactorily pass the requirements, shall remain firm and hard and show no signs of distortion, checking, cracking, or disintegration.

25. **Sulphuric Acid and Magnesia.**—The cement shall not contain more than 1·75 per cent. of anhydrous sulphuric acid ($SO_3$), nor more than 4 per cent. of magnesia ($MgO$).

# NAME INDEX.

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# SUBJECT INDEX.